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ENVIRONMENTAL ASSESSMENT ARCSL-EA-83007

**PROGRAMMATIC LIFE CYCLE ENVIRONMENTAL ASSESSMENT
FOR SMOKE/OBSCURANTS**

VOLUME 4 OF 5 VOLUMES

HC SMOKE

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PREPARED BY

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FOR

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JULY 1983

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US Army Armament, Munitions and Chemical Command
Chemical Research and Development Center
Aberdeen Proving Ground, Maryland 21010

Programmatic Life Cycle Environmental Assessment
for
Smoke/Obscurants


Volume No. 4 of 5 Volumes


HC Smoke

July 1983

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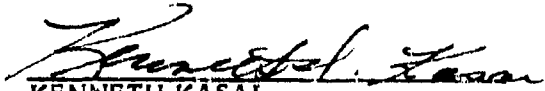

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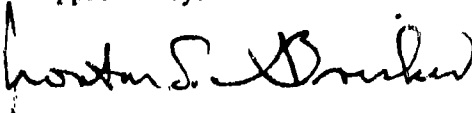
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) HC smoke in pots, grenades, and artillery rounds has been used in military testing and training exercises since the second world war. Research studies conducted to date indicate that HC smoke mix and its combustion products pose significant health hazards to manufacturing personnel and using troops. Therefore, a management plan has been implemented to replace HC smoke with tested, less toxic, noncarcinogenic chemicals. The objective of this report is to compile and review environmental assessment data including environmental impact data on HC smoke — (see reverse) | | |

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along its life cycle usage path from manufacturing to disposal so that mitigating controls may be instituted for the distribution and use of HC smoke until a suitable replacement is implemented into inventory supplies. It is also intended that this programmatic assessment be used and cited in site specific assessments.

It has been concluded that the continued use of present HC inventory stocks should be enforced with such mitigating controls as: (1) enforcing the Army directive to mask in the presence of HC smoke; (2) closely regulating the deployment of HC smoke on all its installations; (3) restricting HC deployment to areas of the installations as far as practically possible from cantonments and other populated areas; (4) taking special precautions to protect higher risk individuals such as those highly allergic, children, and the aged; and (5) under no circumstances should HC smoke be deployed indoors or in confined quarters.

PREFACE

The purpose of this document is to provide a Programmatic Environmental Assessment for HC Smoke Munitions. This covers the life cycle phases for which HC smoke is presently applicable, namely: manufacturing, deployment (testing and training), transport, storage, demilitarization, and disposal. This is volume 4 of a 5-volume series of documents published to provide a general environmental assessment (EA) of the smoke/obscuration program.

Research studies conducted to date indicate that HC smoke mix and its combustion products pose significant health hazards to manufacturing personnel and using troops. Therefore, the Project Manager Smoke/Obscurants, Aberdeen Proving Ground, Maryland, has the responsibility to replace HC smoke with tested, less toxic, noncarcinogenic chemicals. A Project Improvement Program has been started to find a replacement for HC within the 1983-1985 time frame.

Present inventories of HC smoke will be used until replacement stockpiles become adequate. Even with a suitable replacement mix, present inventories are anticipated to remain for several years beyond any implementation date of a replacement. The Project Manager for Smoke/Obscurants is responsible for eliminating any safety hazards from inventory smokes.

This document is not site- or item-specific, however, it is intended to be used as a basic document in the preparation of related life cycle environmental documentation, as well as a major supportive reference for environmental documentation which may have to be prepared for individual site specific operations.

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HC SMOKE

I. PURPOSE AND NEED^{1,2}

As a result of lessons learned from the 1973 Yom Kippur War, considerable emphasis (by both US Army Training and Doctrine Command (TRADOC) and US Army Materiel Development and Readiness Command (DARCOM)) is being placed on the use of smokes/aerosols in combat operations. The 1973 war revealed an urgent need for the development of rapid, visual screening techniques. Even though new smokes are being designed to be effective in the infrared and microwave/millimeter (radar) regions of the electromagnetic spectrum, the visual spectrum, which includes HC smoke, remains an important capability that the Army must have to enhance operations against the enemy. It is believed that the human eye will continue to be the first and most widely used optic system on the modern land battlefield.

The purpose of an HC smoke is to provide the military with a white smoke capability. HC is a pyrotechnic smoke-producing composition of grained aluminum (Al), zinc oxide (ZnO), and hexachloroethane (C_2Cl_6) employed in certain smoke munitions. It is one of two principal agents available in the current inventory to generate "white" smoke, the other agent being white, red, and plasticized white phosphorus. In addition, smoke generators, which use fog oil, are available in reserve forces. HC is also employed in floating smoke pots, which produce large volumes of smoke for extended periods of time on land or water. Pots are the only smoke producing systems that float.

Generally, smoke is not equated to combat power because it is not lethal. Nevertheless, when used correctly, it can significantly reduce the enemy's effectiveness both in the daytime and at night. Smoke, combined with other suppressive fires, will provide increased opportunities for maneuvering forces to deploy, thus enhancing the chances of mission accomplishment without catastrophic losses while operating on the modern battle field. Smokes (and other aerosol obscurants) effectively degrade visual target acquisition systems. Smoke may be used to reduce the ability of the enemy to deliver effective firepower, to hamper hostile operations, and to deny the enemy information on friendly positions and maneuvers. Hence, the importance of smoke agents in support of combat operations has been reinforced. To omit smoke from the planning of modern warfare would create a handicap of major proportions in the next decade.

II. DESCRIPTION OF ACTION

A. Background.

1. The obscuring action of screening smokes is largely due to reflection and refraction of light rays by the individual suspended solid or liquid particles of which the smoke is composed. This action occurs to its fullest extent in the absence of light-absorbing particles such as carbon; white smokes, therefore, have the greatest screening action in the visible spectrum. Actually, white smokes are composed largely of colorless particles, and the white appearance is due to reflection and refraction of all the visible light rays. Smoke screens become more effective as less light passes through. The more the rays are scattered or deviated, the less visual information is transmitted to the observer. During bright daylight, less white smoke than black is required to obscure a target from visible detection.

2. Water vapor in the air plays an important role in the formation of HC smoke; therefore, high relative humidity improves its effectiveness. The water vapor not

only exerts its effects through hydrolysis, but also by assisting the growth to effective size of hygroscopic (deliquescent) smoke particles by a process of hydration. If these particles are too small, they do not effectively scatter light rays and thus do not assist the screening action.

3. Smoke, in general, may be generated by mechanical or thermal means, or by a combination of the two. HC is disseminated by a thermal process. It is vaporized by heat and subsequent cooling condenses the vapor of the solid into minute particles that form the smoke. A chemical reaction accompanies the thermal process and the smoke is not formed until these chemical reactions first take place.

4. HC smoke mix is a solid mixture of grained aluminum, zinc oxide, and hexachloroethane. Zinc chloride is the major component (about 80 percent by weight) generated by burning this HC mixture. Zinc chloride is used in many industries, such as textiles, adhesives and cements, metallurgy, and pharmaceuticals. Hexachloroethane (C_2Cl_6) in its pure state is used in veterinary medicine for the treatment of intestinal worms.^{3,4}

B. History.

Experience during past wars has demonstrated that smoke screens are very effective when properly used. During World War II, extensive use was made of smoke in both defensive and offensive operations. In the intervening years, the use of smoke has been questioned; however, in 1973, the urgent need for the development of rapid, visual screening techniques was reinforced.

During World War I, the first wide-scale use of white phosphorus as a smoke was employed by US Forces. And, at about the same time, a new type of smoke agent was developed (Berger mixture) by CPT Ernest E. F. Berger of the French Army. The mixture contained carbon tetrachloride, powdered zinc, and zinc oxide, and it produced a dense gray smoke of carbon and zinc chloride particles.

Experiment by the Chemical Warfare Service (CWS) with the Berger mixture during the 1920's and 1930's resulted in the replacement of carbon tetrachloride (a liquid) with hexachloroethane (a solid) to decrease evaporation during storage. By 1940 the service was using Type A HC, containing hexachloroethane, zinc, ammonium chloride, and ammonium or potassium perchlorate, as a filling for smoke pots and other munitions. The fall of France cut off America's supply of imported perchlorate, and chemists substituted calcium silicide. The new mixture (designated as Type B, HC) functioned satisfactorily, but industrial firms had trouble producing it. It was found that calcium silicide could be a dangerous material. When it was ground to a powder, it reacted rapidly with oxygen in the air, sometimes causing an explosion. The danger led to the development of a safer mixture, Type C, HC, containing grained aluminum, hexachloroethane, and zinc oxide, which is still employed today. Shells, grenades, and bombs were employed during the war, but by far the most widely used HC munition was the smoke pot.

Because of immediate smoke release, smoke pots are useful in setting up a preliminary screen during the five or so minutes that it takes large mechanical generators to warm up and start functioning. Pots helped to shield harbors and installations on the coast of North Africa, as well as the harbors of Palermo, Licata, and Porto Empodocle on Sicily. The small size and light weight of pots enabled troops to carry them ashore and employ them until heavy, bulky, mechanical generators could be

landed. After Salerno, smoking of invasion areas by army units and by naval support boats became a standard practice in both the European and Pacific theaters of operation.

In Italy, pots also graduated from harbor defense and invasion defense to use in forward areas. Troops employed them to screen supply routes, bridge construction, river assault crossings, tanks, ammunition dumps, troop concentrations, ground operations, and even to hide mortar flash.

The Army and Navy employed floating smoke pots to screen amphibious operations from enemy observation and artillery fire. Harbor defense units needed floating pots to assist in maintaining smoke rings against enemy planes.

The Third Army in its drive across France into Germany employed thousands of floating pots in assault river crossings, bridge construction, ferry operations, and other missions. The Ninth Army employed several thousand pots in crossing the Ruhr and Rhine rivers. Other armies set up floating screens whenever the occasion demanded. Since floating pots functioned on land as well as on water, troops often employed them in place of standard land pots when supplies of the latter ran low.

For these reasons the CWS undertook the development of this type of munition in 1942. The final model of the floating pot, designated as M4A2, was ready in March 1944 and remains in the Army's inventory today.

C. Modes of Dissemination vs Munition Types.

1. Description.

The munitions currently used to disseminate HC smoke include the 155-mm and 105-mm artillery rounds, M1 and M5 land smoke pots (Figures 1 and 2), M4A2 floating smoke pot (Figure 3) and the M8 Smoke Grenade (Figure 4). These munition types are characterized in Table 1.

a. Artillery rounds are used to deliver smoke on distant targets in both offensive and defensive deployment roles.

b. Smoke pots can be grouped together (Figures 5 and 6) to produce large volumes of smoke for extended time ranges. These pots can be emplaced by hand or dropped from vehicles and helicopters and ignited manually or by remote electronic signal. The land pots, as the name suggests, are used on land; however, floating pots can be used on land or water.

c. Smoke grenades are emplaced by hand primarily to cover or screen individual vehicles.

Product Improvement Programs are currently in process to replace HC smoke in all the above mentioned munitions with less toxic mixes such as red phosphorous.

The floating M4A2 smoke pots may remain in the Army inventory longer than the other munition types (Table 1) since a suitable replacement has not been successfully demonstrated as reliable for deployment over water.

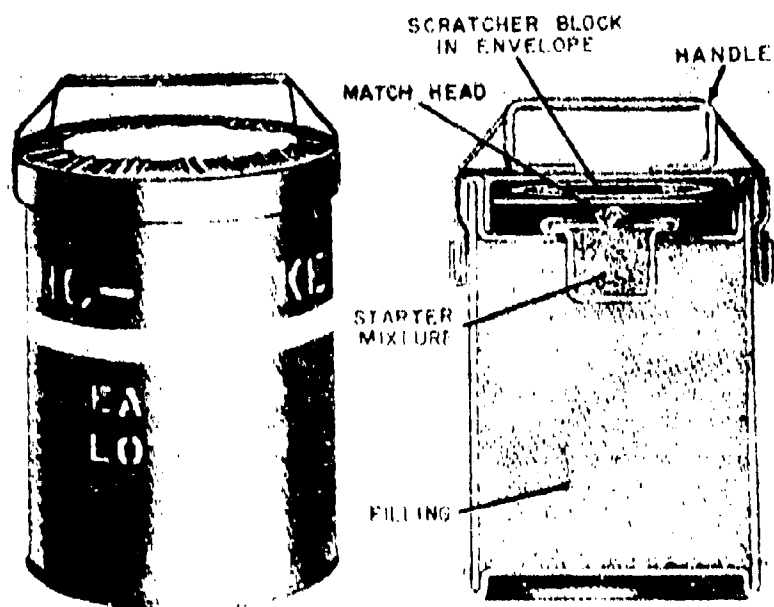


Figure 1. M1 Ten-Pound HC Smoke Pot

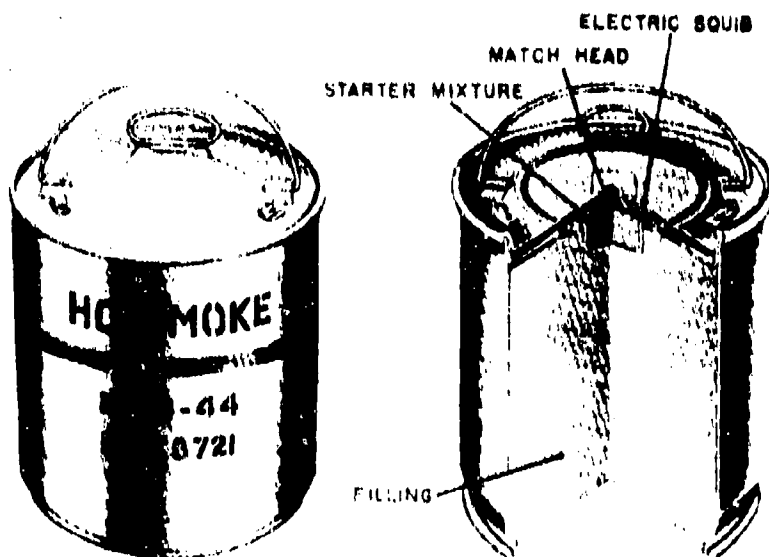


Figure 2. M5 Thirty-Pound HC Smoke Pot

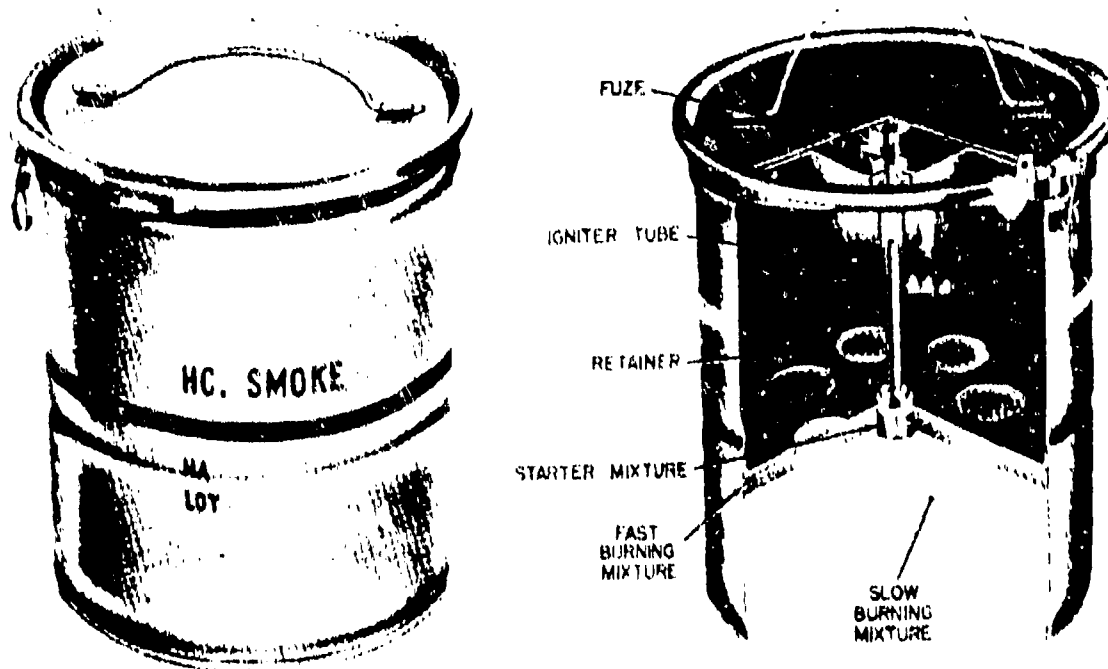
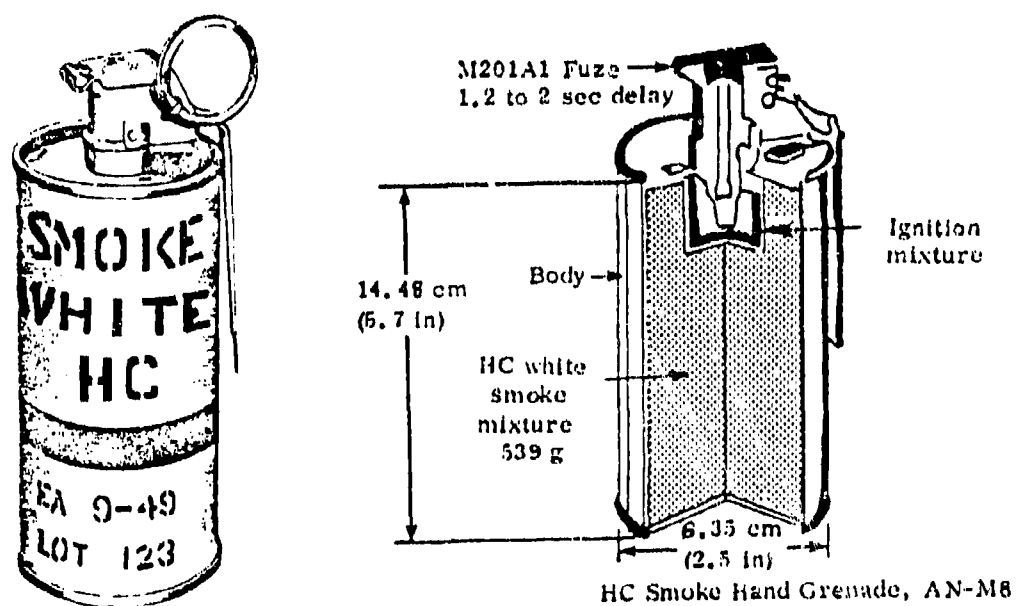


Figure 3. M4A2 HC Floating Smoke Pot



GRENAD, HAND, SMOKE, HC, AN-M8.

Figure 4. M8 HC Smoke Grenade

Table 1. HC Smoke Munitions

| Smoke pot munition | Container size (in.) | Filling | | Ignition method | Weight (lb) (approx) with fuze | Delay time (sec) | Burning time (min) | Remarks |
|--------------------------------------|----------------------------|----------------------------|---------------------------------|---|---|------------------------|--------------------------|---|
| | | Weight (lb) (approx) | Material | | | | | |
| Smoke Pot, HC, 10-lb, M1 | 9 by 5.5 dia | 10 | Type C** HC smoke mixture | Matchhead and scratcher block or electrical | 12.5 | 10 | 5-8 | |
| Smoke Pot, HC, 30-lb, ABC-M5 | 9.5 by 8.5 dia | 31 | Type C HC smoke mixture | Matchhead and scratcher block or electrical | 33 | 20-30 | 12-22 | |
| Smoke, Pot, floating, HC, M4A2 | 13 by 12 dia | 27.5 | Type C HC smoke mixture | M207A1 smoke pot fuze | 38 | 10-20 | 10-15 | |
| Smoke Grenade, HC, M8 | 4.75 by 2.5 dia | 1.2 | Type C HC smoke mixture | M201A1 fuze | 1.5 | 0.7-2* | 1.7-2.5 | *Time to functioning after release of safety lever |
| Cartridge, 105-mm, HC M84A1 | | 12.3 | Type C HC smoke mixture | Mechanical Time & Super Quick fuze | 13.0 | 60-90 | 3 | No future production for the M84A1 is planned as of this writing |
| Projectile, 155-mm HC, M116A1 | | 25.8 | Type C HC smoke mixture | Mechanical Time & Super Quick fuze | 26.2 | 60-90 | 4 | M116A1 is presently completing its production life cycle and will be replaced by future pro- duction of XM 823 - white phosphorus fill |

*TYPE C HC smoke contains grained aluminum, hexachloroethane and zinc oxide. Reference History section for the details on types A and B used in the early years of smoke generation.

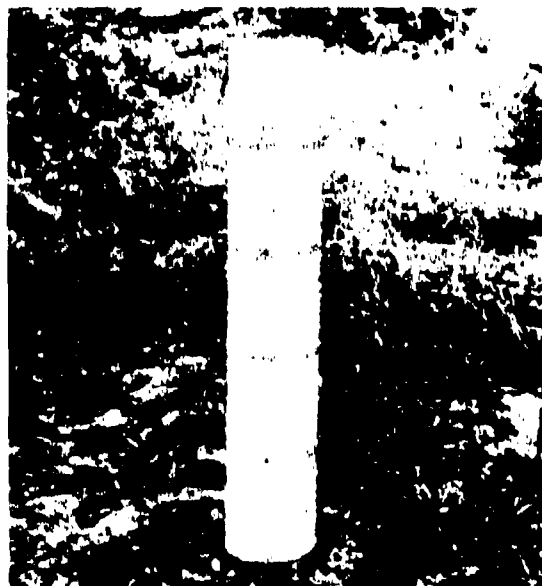


Figure 5. M5 Smoke Pots
Stacked Vertically.

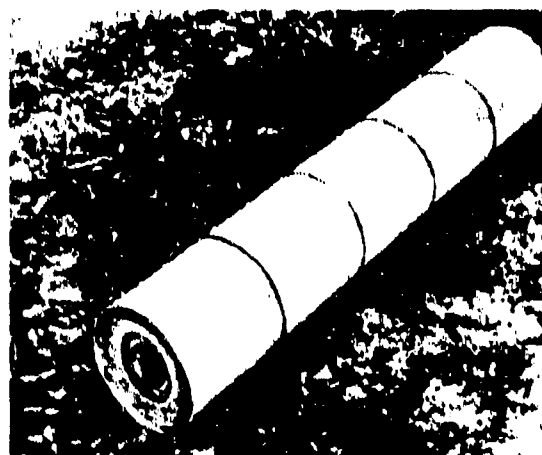


Figure 6. M5 Smoke Pots
Laid End to End.

2. Ignition Techniques.

The initial heat needed to start the burning of an HC smoke mixture is provided by a pyrotechnic starter mixture which is ignited either manually or electrically. Smoke pots, unlike artillery and grenades, can be stacked together for multiple or chain ignition and ignited simultaneously at different locations, therefore, employing both manual or modified electric ignition.

D. Description of HC Smoke.

1. Smoke Mix Properties.

a. Composition. HC smoke is made up of a mixture of grained aluminum (Al), zinc oxide (ZnO), and hexachloroethane (C₂Cl₆). Percentages by weight of HC smoke mixture (type C) are as follows:

| <u>Ingredient</u> | <u>Percent (approx)</u> |
|-------------------|-------------------------|
| Grained aluminum | 6.68 |
| Zinc oxide | 46.66 |
| Hexachloroethane | 46.66 |

The ratio of zinc oxide to hexachloroethane is held between the limits of 1.04 and 1.00, but the aluminum may be varied slightly to regulate the burning time, as illustrated:

| <u>Aluminum content (percent)</u> | <u>Burning time (seconds)</u> |
|-----------------------------------|-------------------------------|
| 9.0 | 55 |
| 8.4 | 64 |
| 8.0 | 65 |
| 7.5 | 71 |
| 7.0 | 84 |
| 6.5 | 96 |
| 6.0 | 107 |
| 5.5 | 147 |

In certain munitions, such as pots, an upper and lower layer of mix are used in a standard container. The only difference between layers is the aluminum content. A larger percentage of aluminum in the upper layer induces a faster and hotter reaction and facilitates initiation of the reaction in the lower layer.

The principal impurities in the above reagent mix are cadmium and lead, which vary widely from lot to lot. Trace constituents include mercury and arsenic.

Table 2 is a summary of characteristics derived from tests designed to evaluate the properties of HC smoke mix.

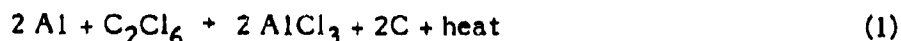
Table 2. Summary of Parametric, Stability, and Sensitivity Data for HC Smoke Mix

| | | <u>HC</u> |
|---------------------------|-------------------|----------------|
| Autoignition temperature | °C | 167 |
| Decomposition temperature | °C | 193 |
| Density (bulk) | g/cm ³ | 1.14 |
| Density (loading) | g/cm ³ | 1.6-1.9 |
| Fuel/oxidizer ratio | x:1 | 0.2 |
| Heat of combustion | cal/g | 940* |
| Hygroscopicity | 90% | Fair |
| Thermal stability | 75°C | Poor |
| Vacuum stability | ml/gas/40 hr | 0.24 |
| Card gap | | Strong shock** |
| Detonation test | | Mild shock** |
| Electrical spark | Joules | 0.122 |
| Friction | | Insensitive |
| Impact sensitivity | Inches | 10 |
| Burn time | sec/cm | 9.8 |
| Critical diameter | meter | 1 |
| Critical height | cm | 218 |
| TNT equivalency | % | 0 |

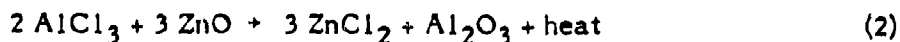
*The maximum heat of combustion was 940 cal/g. From other test observations and calculations the range for heat of combustion seems to vary from a low of 300 cal/g to 940 cal/g.

**HC smoke mix is sensitive to electrical spark, moderately sensitive to impact, and insensitive to friction, strong shock in the card gap test, and mild shock from a number 8 blasting cap in the detonation test. HC smoke failed to burn when exposed to open flame in an ignition and unconfined burning test.

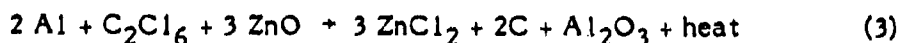
b. Chemical Reaction. When the HC smoke mixture is heated, a propagating reaction is set up which is based, in part, upon the tendency of aluminum to split chlorine from chlorinated hydrocarbons, such as hexachloroethane, and from aluminum chloride as illustrated in the following equation:



The AlCl_3 reacts with ZnO to form ZnCl_2 , as illustrated in the following equation:

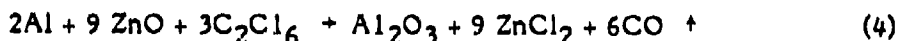


A general summarizing reaction can be written:



ZnCl_2 leaves the reaction zone as a hot vapor and, on cooling below the condensation point of ZnCl_2 , produces the desired aerosol.

By reducing the aluminum content, but keeping the proportions of hexachloroethane and zinc oxide constant in the smoke mixture, the amount of carbon appearing in the smoke is reduced, thus making the smoke whiter and diminishing the burning rate. The reaction where no carbon is liberated is:



The amount of aluminum in the above reactions can be varied from 3.6 to 10.1 percent. When the aluminum content is reduced below 5 percent, however, the burning time becomes erratic and other means must be employed to regulate the burning. For this purpose, basic zinc carbonate in a quantity not exceeding 7 percent of the zinc oxide is used.⁶

Zinc chloride is vaporized in the hot reaction and, on cooling below the condensation point, nucleates to form the aerosol that absorbs water rapidly from the surrounding atmosphere to produce a particle size distribution ideal for attenuation of the visible spectrum. Small amounts of aluminum chloride (AlCl_3) and hexachloroethane (C_2Cl_6) are lost as vapor. In a differential thermal analysis of the reactions between hexachloroethane and zinc oxide, the data suggested the formation of carbon tetrachloride (CCl_4), ethylene tetrachloride (C_2Cl_4), phosgene (COCl_2), and a zinc oxychloride ($2\text{ZnO} \cdot \text{ZnCl}_2$).⁷

c. Starter Mix. HC smoke pots utilize a pyrotechnic starter mix to provide the initial heat to get the mixture well ignited. The following mixture is typical: silicon, potassium nitrate, charcoal, iron oxide, grained aluminum cellulose nitrate, and acetone. This mixture has some of the burning properties of both thermite and black powder.

d. Reaction Products. Reaction products are composed of gaseous and aerosol products as follows:

Gaseous Reaction Products.

It has been concluded from field testing and laboratory experiments that HC combustion results in the formation of the following RXN (reaction) products:⁶

carbon monoxide (CO), hydrogen chloride (HCl), carbonyl chloride or phosgene (COCl_2), carbon tetrachloride (CCl_4), ethylene tetrachloride (C_2Cl_4), hexachlorethane (C_2Cl_6), hexachlorobenzene (C_6Cl_6), and chlorine (Cl_2).

Quantitatively, the percentages indicated below do not contain a high degree of confidence because of the limited testing conducted to date. They are just presented as an indicator of what amounts might be expected from smoke generations. The most abundant in the laboratory tests was C_2Cl_4 , 3-17% of the reagent weight under various reaction conditions, followed by CCl_4 (1-3%), C_2Cl_6 (0.3-0.5%), COCl_2 (0.1-1%), and C_6Cl_6 (0.4-0.9%). The percentages for HCl and CO are not included as it was determined that the results were probably compromised by the interval of time between sample collection and analyses.

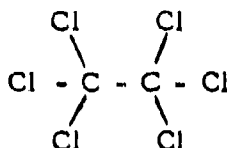
Aerosol Reaction Products.

The aerosol particle is predominantly zinc chloride, approximately 80 percent by weight of the products of the HC smoke mix, with small amounts of aluminum chloride (AlCl_3), and traces of lead and cadmium chlorides.^{7,8}

2. Properties of Hexachloroethane (C_2Cl_6).

Alternate Names.

Hexachloroethane (the constituent of HC mix) is a chlorinated hydrocarbon possessing the following chemical structure.



The molecular formula of this compound is C_2Cl_6 corresponding to a molecular weight of 236.74 g/mole. The pertinent alternate names for hexachloroethane are:

CAS Registry No. 67-72-1

CA Name (8Cl) - Ethane, hexachloro

Wiswesser Line Notation: GXGGXGGG

Synonyms: Avlothane; Carbon hexachloride; Distokal; Distopan; Distopin; Egitol; Falkitol; Fasciolin; Hexachlorethane; Hexachloroethane; Mottenhexe; Perchloroethane; Phenohep

Physical Properties.

The physical properties of hexachloroethane* are:

| | |
|-----------------------------|--|
| Physical form @ 20°C: | solid |
| Color and crystalline form: | colorless rhombic |
| Odor | camphor like |
| M.P. | 186.8°C (triple point - sublimes simultaneously) |
| Crystal density | 2.09 |
| Vapor density (air=1) | 6.3 g/l @ 186.8°C |
| Specific heat @ 20°C | 0.266 cal/g/°C |
| Heat of vaporization | 46 cal/g |
| Vapor pressure @ 32.7°C | 1 mm Hg |
| Solubility | water: insoluble soluble in alcohol, benzene, toluene petroleum solvents, chlorinated solvents |

E. Effects of Climatic and Geologic Conditions on Dispersion Clouds.

The effects of weather, particularly wind speed and direction, and terrain conditions are important factors to be considered in smoke screening operations. The movement of smoke depends upon the speed and direction of the wind. Wind direction and velocity are important factors in estimating the amount of smoke required. Other factors to be considered are: temperature, temperature gradient, humidity, precipitation, and cloud cover. The details associated with these meteorological and geological factors for determining and planning screening/dispersion scenarios are included in Appendix A.

F. Dissemination Models.

1. HAZARD2.

A computer data base has been developed to aid users in the predictions of environmental impact and hazard effects as a result of smoke deployment. This computer program entitled HAZARD2 was developed by the Chemical Systems Laboratory, ARADCOM for use on the Univac 1100/60 computer, located at the Edgewood area of Aberdeen Proving Ground, through remote terminals.

The objective of this effort was to develop and document a computer program to predict downwind dosages of aerosol materials resulting from the operation of one or more dissemination devices during either training or testing exercises. Basic program outputs include total dosage as a function of downwind distance, total area for the dosages of interest, and a graphic display of dosage contours.

*Rhodia, Inc. (the current supplier of hexachloroethane), 1978.

Worse case predictions or actual effects can be determined by inserting intended locational test/training HC input conditions.

Interested persons can be provided user documentation.

A sample computer graphic display (output) is shown in Figure 7.

The input variables in this example were:

- Location - Nondefined (worst case)
- Season - Summer
- Munition type - Smoke
- Munition - M5
- Agent - Hexachloroethane (HC)
- Relative Humidity - zero %
- Wind (m/sec) - 6.0
- No. rounds - 41

Although this example is specific for M5 smoke pots, any HC munition can be applied to the model.

III. ENVIRONMENTAL LAWS AND REGULATIONS

Environmental laws and regulations are of two types: 1) those requiring assessment of environmental impacts of specific programs or actions, and 2) those requiring compliance with environmental pollution standards. The chemicals and facilities associated with smoke operations may be affected by one or more of the statutory requirements listed below. The primary purpose of this section is to identify the general features and applications of those environmental regulations most likely to influence smoke operations during their life cycle. Specific applications will vary with individual items, and should be addressed accordingly.

A. National Environmental Policy Act (NEPA):

The National Environmental Policy Act (NEPA) of 1969 was created by Congress to establish a national policy for protection of the environment and to provide the goals and means to avoid or minimize adverse environmental consequences by requiring that impacts of planned federal actions and alternatives be evaluated before being undertaken. As currently amended this act is binding on activities of all federal agencies, except where inconsistent with other statutory requirements. Certain provisions of NEPA are also incorporated into other federal legislation, including the National Historic Preservation Act of 1966 and the Endangered Species Act of 1973.

Army policy in NEPA matters is provided in AR 200-2, which establishes responsibilities and procedures for integration of environmental considerations into Army planning and decision making. Among these responsibilities are the identification and analysis of environmental risks for proposed actions and their most likely alternatives. DARCOM policy requires environmental analysis and documentation for all items (including smokes) being developed under its program/project/production managers and research and development commands.

DOSAGE CONTOUR HALF-WIDTHS

LOC: NOF SERS: SUM MULTIP: SMOKE
 MUN: MS PAN: HC STB: D

REL HUMIDITY (PERCENT): .000 WIND(M/SEC): 6.00

NO. RND: 41 DIST: 5 PARAM A(M): .00 PARAM B(DEG): 1.57

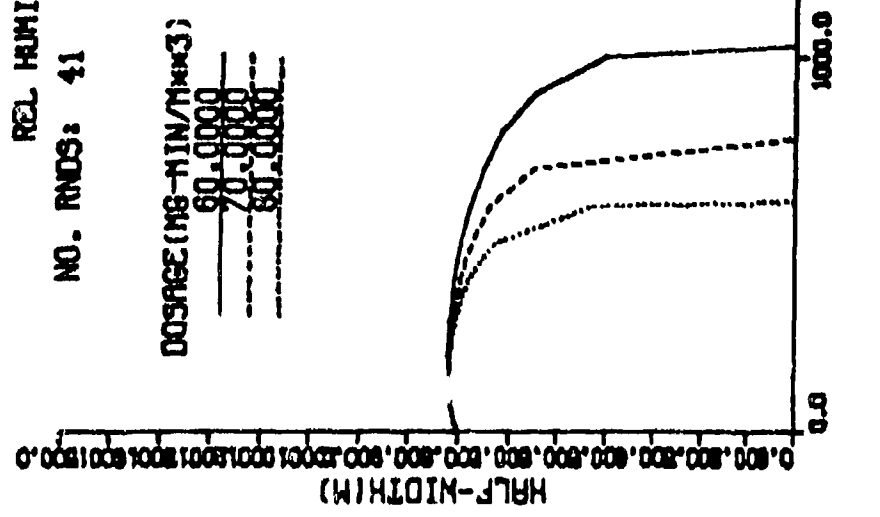


Figure 7. HC Smoke -- "Sample" Computer Output --
 Graphics Terminal

B. Resource Conservation and Recovery Act (RCRA).

The Resource Conservation and Recovery Act (RCRA) of 1976 established a national program for management of waste, including hazardous waste (40 CFR parts 260 thru 264 and 266 thru 267). Wastes are defined by RCRA as "hazardous" (1) if specifically listed by regulation, or (2) if exhibiting any one of the characteristics of reactivity, corrosivity, ignitability, or EP toxicity (as defined in 40 CFR, 261.2). The present EPA list includes approximately 400 chemicals and 85 process wastes. State and local regulatory authorities may administer hazardous waste management programs provided that the programs are at least as stringent as the federal program. Therefore, state and local programs should be evaluated for consistency with the federal regulations.

Under RCRA, the originator of waste has the responsibility for determining whether or not it is hazardous. If found to be hazardous, the waste is then subject to comprehensive "cradle to grave" record keeping requirements, including a manifest system to track and document the generation, transportation, and ultimate disposal of the material. It should be emphasized that substances are not classified by RCRA as wastes until they are ready to be discarded (i.e., regulations do not apply if substances - otherwise classifiable as wastes - are recycled for other industrial purposes).

The following HC smoke constituents are listed under RCRA (Title 40 CFR part 261.33). Items listed as hazardous wastes are not considered a hazardous waste until they are finally identified for disposal in accordance with DARCOM Supplement No. 1 to AR 200-1.

1. Hexachloroethane (C_2Cl_6) is a listed hazardous waste constituent, Item U131, and thus regulated for disposal as opposed to training.

2. Phosgene ($COCl_2$) is a by-product of HC smoke and listed as acutely hazardous, Item P095.

3. Carbon tetrachloride (CCl_4) is a by-product and listed as a hazardous waste constituent, Item U211.

4. Hexachlorobenzene (C_6Cl_6) is also a by-product and listed as a hazardous waste constituent, Item U127.

C. Toxic Substance Control Act (TSCA).

The Toxic Substance Control Act (TSCA) of 1976 addresses the manufacture, importation, distribution, and use of chemical substances. As amended (40 CFR, parts 704-710), this act authorizes the Environmental Protection Agency (EPA) to inventory commercial chemicals and requires sufficient data to estimate health and environmental hazards of production use for chemicals listed after 31 December 1979.

Present HC smoke mix materials were inventoried on the initial TSCA Inventory list.

D. Clean Air Act (CAA).

The Clean Air Act of 1963 was created because of public concern over health problems associated with air pollution. As currently amended, (40 CFR, parts 50-52), the Clean Air Act established National Ambient Air Quality Standards (NAAQS) for the control of criteria air pollutants to prevent adverse effects to air resources, human health, and the environment. The NAAQS most likely to affect the smoke program are presented in Table 3. However, it is likely that a NAAQS would only affect smoke generation if it occurred frequently, on a large scale, and in the same general location. It is more likely that smoke generating exercises would exceed certain emission standards/nuisance laws established by state and local regulatory agencies. State and local municipalities may adopt standards that are more stringent than the NAAQS, and local standards should be evaluated for consistency with national standards. Until recently, the emission of hydrocarbons was regulated by an NAAQS; however, on 30 December 1982, the NAAQS for hydrocarbon was rescinded by the EPA. According to the EPA, because no consistent quantitative relationships between concentrations of ambient air ozone and hydrocarbon air quality levels could be found to exist, the original basis for the standard could not be justified.

The generation of smokes/obscurants impact directly on local air quality. The quality of air is protected by federal, state, and local air pollution control regulations. Under the CAA, the country is divided into 247 air quality control regions (AQCRs) to provide basic geographical units for air pollution control. States are required to prepare State Implementation Plans (SIPs) to implement and enforce criteria pollutant standards in those regions. AQCRs that have attained the NAAQS for a criteria pollutant are considered to be in "attainment" for that pollutant. AQCRs in violation of NAAQS for a criteria pollutant are considered "non-attainment" for that pollutant. Most standards specify two types of limitation - long term standards which cannot be exceeded on an annual average and short term exposures which cannot be exceeded for brief periods (e.g., 3 hours and/or 24 hours). Because the deliberate generation of smokes during testing or training is directly counterproductive to the air pollution abatement and control efforts of the environmental regulatory agencies, the Army environmental coordinator at the individual test or training site should be consulted to determine whether a particular activity is regulated and to coordinate the smoke exercise with regulatory agencies for permits or variances, as required. Among the gaseous products of HC smoke is phosgene. When hexachloroethane (C_2Cl_6) is heated to decomposition, it emits highly toxic fumes of phosgene and zinc chloride. Both could present potential air pollution hazards if they are emitted frequently, on a large scale, and in the same general location.

E. Federal Regulations Governing Hazardous Substance Release into the Environment.

Policy and procedures for control of discharges of hazardous substances into the environment are detailed in Federal Water Pollution Control Act (FWPCA)*

*FWPCA is commonly known as the Clean Water Act.

Table 3. Federal Ambient Air Quality Standards for Certain Criteria Pollutants

| Chemical | National standards |
|--------------------|--|
| Particulate matter | (A) 75 $\mu\text{g}/\text{m}^3$ annual geometric mean (B) 260 $\mu\text{g}/\text{m}^3$ - maximum 24 hour concentration not to be exceeded more than once per year |
| Ozone | 0.12 ppm (235 $\mu\text{g}/\text{m}^3$). The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 parts per million (235 $\mu\text{g}/\text{m}^3$) is equal to or less than 1.0 |
| Hydrocarbons | EPA Standard Rescinded |

(PL95-576) and the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) (PL96-510). Section 311 of the FWPCA describes requirements for handling discharges of hazardous substances into or upon navigable United States waters, adjoining shoreline, or the contiguous zone which may effect US natural resources.

EPA has promulgated regulations under the FWPCA which identify and establish reporting requirements for approximately 270 hazardous substances. Reporting requirements are based on harmful quantities as defined by the regulation. Zinc chloride, the predominant aerosol product of HC smoke, is included on the FWPCA hazardous substance list.

A Spill Prevention and Countermeasure Control (SPCC) Plan and an Installation Spill Contingency Plan (ISCP) establish procedures to prevent spills and to ensure prompt reporting, containment, and cleanup of spills should they occur. Reporting procedures for spill events are outlined in Army Regulation 200-1, Chapter 8, 15 Jun 82.

Since HC is not liquid and not subject to spill, per se, the plan should refer to leakage as leakage from the munitions mix.

The CERCLA also establishes reporting requirements for the release of hazardous substances into the environment, including land, air, and water when release occurs in amounts equal to or greater than the reportable quantity. A hazardous substance as defined by CERCLA includes any substance designated or listed in: FWPCA, Section 307 and 311; RCRA, Section 3001; CAA, Section 112; and TSCA, Section 7. The "reportable quantity" for any hazardous substance is 1 pound, unless otherwise specified in Section 311 of the FWPCA. The reportable quantity under CERCLA for zinc chloride is 5000 (2270 kg) lb or more per 24-hour period. A reportable quantity for HC is not listed unless it actually enters a waterway as an unauthorized discharge in the parameter quantities listed in 40 CFR Table 117.3.

F. Hazardous Materials Transportation Regulations.

1. Department of Transportation Regulations.

The Department of Transportation (DOT) is required by federal law to formulate regulations for safe transportation of hazardous materials, poisonous substances, explosives, and other dangerous articles (Title CFR 49, parts 171-177). These regulations bind all carriers engaged in the transport of the above mentioned hazardous material and are in accordance with the best known practices for assuring safety in transit. Of particular importance is part 172 of these regulations, which lists hundreds of materials by hazard class (e.g., "flammable," "corrosive") with guidelines for safe packaging and shipping.

HC smoke munitions are classified as Class C explosives. Hexachloroethane (C_2Cl_6) or HC mix has separate packing regulations when it is shipped by itself. Table 4 lists the hazard class and labels for HC smoke munitions.

2. Military Regulations.

Explosives and other dangerous articles shipped or transported by the military services are subject to the applicable regulations of the military service involved. Modes of transportation covered by the regulations are:

a. Surface Carriers.

AR 55-355 regulates the movement of military cargo within the United State by commercial vehicle.

b. Air Shipments.

Air shipments are regulated by TM 38-250 which covers safe transport of hazardous articles.

c. Water Shipments.

AR 55-228 regulates shipment and transport of dangerous and hazardous articles by water in conjunction with US Coast Guard regulations.

3. Other Regulations.

a. In addition, there are state, county, and local laws governing the transportation of flammables and hazardous materials and ordinances regulating the transportation of hazardous articles within these subdivisions.

b. Policies and procedures for environmental protection on military installations are provided in AR 200-1, "Environmental Protection and Enhancement," plus respective supplements.

Table 4. DOT Hazardous Materials (9 CFR 49, 172.101)

| Name | Hazard class | Identification no. | Labels required | Packing section of CFR 49 | Maximum net quantity |
|---|-------------------|-----------------------|--------------------|------------------------------|---|
| Hexachloroethane (C ₂ Cl ₆) or HC mix | ORM-A | NA 9057 | None | 173.650 | ----- |
| HC smoke grenade | Class C Explosive | - | Explosive C | 173.108 | 50 lb, passenger aircraft 150 lb, cargo aircraft |
| HC smoke pot | Class C Explosive | - | Explosive C | 173.108 | 50 lb, passenger aircraft 200 lb, cargo aircraft |

Note: No future production for 105-mm HC cartridges and 155-mm HC projectiles are planned. The 105-mm cartridges will not be produced, and the 155-mm HC projectile is being replaced by future productions of XM825 white phosphorus fill.

G. Storage Regulations for Hazardous Materials.

For ease of storing and handling, chemical agents are divided into chemical groups. Classification is based on the action of the item, and the degree and type of protection required. In accordance with DARCOM-R 385-100, HC smoke and munitions are assigned Chemical Group B and storage compatibility Group G. Reference Table 5 for clarification.

H. Other Consideration.

1. Regulations on endangered species or historic preservation are primarily site specific. The environmental quality coordinators of the installation should be contacted to determine if these regulations are applicable.

2. The Department of the Army (DA), DARCOM, and TRADOC prohibit open burning of HC smokes. DARCOM policy as outlined in DARCOM Supplement 1 to AR 200-1, Chapter 4, para 4-4f, states that the open burning of HC, white phosphorous (WP), and colored smokes is prohibited. Requests for exception to this policy should be forwarded to Commander, DARCOM, ATTN: DRCSG, with appropriate justification.

IV. TOXICITY AND HEALTH EFFECTS

A. Introduction.

Human, animal, and aquatic toxicity data from US Army Medical Research and Development Command Reports^{3,4,7,9,10} are summarized in Appendix B of this document.

Toxicity data is not available for all the constituents of HC smoke. The following is a list of those for which information has been derived and/or those items which have been singled out as being the major health concerns for army workers and/or using troops:

1. HC Smoke Mix. This mixture consists of grained aluminum, hexachloroethane, and zinc oxide. Medical research indicates hexachloroethane (C_2Cl_6) as the component to control for workers involved in handling or working around HC mix. C_2Cl_6 is classified under RCRA as a hazardous waste constituent and has been found to be carcinogenic to some animals.

2. Combustion By-Products. Zinc chloride ($ZnCl_2$), the major constituent of HC smoke, is a potential hazard to personnel involved in testing or training and to the environment. The less pronounced by-products of phosgene, carbon tetrachloride, and hexachlorobenzene are characterized under RCRA as hazardous or toxic waste products.

B. Human (Mammalian).

1. HC Smoke.

HC smokes are used in Army training. They have been employed to some extent every year since the second world war. In 1981 alone, TRADOC installations

Table 5. Storage Information and Shipping Classification^a

| Agent symbol | Common name | Action of agent | Visual ID | Chemical group | Storage compatibility group | DOT hazard class | Color coding identification |
|------------------|--------------------------------------|-----------------|-------------|----------------------|-----------------------------|------------------|--|
| HC smoke mixture | Aluminum zinc oxide hexachloroethane | Smoke | White solid | Group B ^b | Group G ^c | Flammable solid | LIGHT GREEN base coat; HC & other information in BLACK |

NOTE: The same group designation that is used for chemical materials, i.e. HC smoke mix, shall be used for chemical munitions, namely, HC smoke grenades and HC smoke pots. The chemical and storage compatibility groups of the munition item shall be the same as that of the chemical material contained in the item.

^aDARCOM-R 385-100 (17 August 1981)

^bChemical Group B - shall include materials (gaseous, liquids or solids) which are toxic or incapacitating by inhalation, ingestion or percutaneous absorption. Wearing of suitable respiratory protection is required for the protection against inhalation of vapors, particles or smoke from burning agents.

^cStorage Compatibility Group G - Ammunitions that, upon functioning, result in smoke etc.

detonated 125,000 HC munitions.* These smokes are also used each year in testing scenarios.

Acute exposure to high concentrations (80 - 120 mg/m³ for 2 minutes) of HC smoke produces an immediate sense of suffocation, with irritation of the nose and throat and coughing and choking. This may be followed by bronchial to low constriction, with symptoms similar to those of asthma. Prolonged exposure to low concentrations causes an elevation of temperature, moderate inflammation of the pharynx and conjunctivae, pain in the chest on deep inspiration, headache, slight cough, malaise, and muscular pains. Severe exposure induces nausea and vomiting, dyspnea cyanosis, and signs and symptoms of chemical pneumonitis and pulmonary edema.

The initial charge of most HC smoke contains C₂Cl₆ (46%), ZnO (46%), and fine-grained Aluminum (5-8%). The ZnO is contaminated with trace quantities of cadmium and lead. Arsenic and mercury were also detected as contaminants.

Gaseous products of the smoke-generating reaction include hexachloroethane, hexachlorobenzene, ethylene tetrachloride, carbonyl chloride, carbon tetrachloride, carbon dioxide and monoxide, and traces of phosgene.

The Army knows very little about the toxicity of these compounds to humans and environment during training and testing. Some of the training areas may be located adjacent to fishing ponds, hunting areas, areas leased for grazing beef and milk cattle, or off-post housing and/or cantonment areas. Although something is known about the toxicity of each of the individual compounds, little is known about the fate of these compounds in combination with each other under actual deployment circumstances or the possible synergistic or antagonistic effects on living organisms.

Hexachloroethane (C₂Cl₆) is fairly toxic to mammals. The LDLO for intravenous administration to dogs is 325 mg/kg and to rabbits by subcutaneous administration, 4000 mg/kg.¹¹ It can be absorbed from the gastrointestinal tract, through the lung, and through the skin.

There has been some experience in industry to indicate that an excessive amount of hexachloroethane dust in the air can cause irritation. Fumes of the material when handled hot have been reported to be moderately irritating to the skin and mucous membranes. The dust has been assigned a moderate hazard rating that may involve both irreversible and reversible changes, but not severe enough to cause death or permanent injury. Liver injury has been described from exposure to this material. The dust is given a slight explosive hazard rating, but is considered a dangerous disaster hazard since, when heated to decomposition, it emits the highly toxic gas phosgene. Others note that hexachloroethane is very toxic, causing more potent central nervous effects than chloroform or carbon tetrachloride, but slower in action. On ingestion, it was reported that severe mucosal injury and often liver necrosis occurs.¹²

*Letter, Construction Engineering Research Laboratory, Corps of Engineers, Champaign, Illinois, subject: "Proposal on Use of Hexachloroethane Smokes in Training," 29 April 1982.

Male and female mice that received doses of 1179 mg/kg/day of C_2Cl_6 by oral gavage developed hepatocellular carcinoma.¹²

Uses of hexachloroethane in the US are as: (a) a constituent of candles and grenades for the generation of smoke or fog; (b) a degassing agent for magnesium; (c) a component of extreme pressure lubricants; (d) an ignition suppressant in combustible liquids; (e) a moth repellent; (f) a plasticizer for cellulose esters; (g) an anthelmintic in veterinary medicine; (h) an accelerator in rubber; (i) a retardant in fermentation processes; (j) a component of submarine paints; (k) an additive to fire-extinguishing fluids; and (l) a constituent of various fungicidal and insecticidal formulations. Only limited quantities are used in these applications. The major use in Japan is for degassing in the aluminum casting industry.

2. Zinc Chloride Effects.³

Most of the published toxicity data in connection with HC smoke is on zinc chloride ($ZnCl_2$), the prime aerosol constituent of HC smoke. Zinc chloride is included on the FWPCA hazardous substance list. It has been used in the military as a smoke screen, but is also used in galvanizing, welding, textiles, wood preserving, and in other industries.

Zinc chloride smoke is a potential health hazard, especially when generated in an enclosed space with inadequate ventilation. Persons breathing in high concentrations suffer severe pulmonary irritation. The lungs can become filled with fluid and the lung tissue may be destroyed. Extended exposure to high concentrations can be fatal. Skin contact with aqueous zinc chloride solutions causes severe burns especially if contact occurs around a pre-existing wound. Oral intake of zinc chloride has produced corrosive gastritis and liver necrosis. Eye and nose contamination with zinc chloride has caused burns on the eyes, permanently impaired vision, and permanent loss of the sense of smell.³

Laboratory dogs exposed to high concentrations of zinc chloride smoke developed fluid in their lungs. Application of a solution of zinc chloride to the shaved skin of guinea pigs slowed growth but did not cause deaths. However, an injection of a zinc chloride solution into the abdomens of guinea pigs caused the deaths of 8 out of 10 animals in one week; 6 died within 24 hours. Prolonged oral intake of a solution of zinc chloride in addition to a diet deficient in pantothenic acid, caused symptoms of vitamin deficiency and retarded growth in rats. In another study, prolonged oral intake of zinc chloride did not affect reproduction, and normal young were born. Rats subjected to intraperitoneal injections of zinc chloride, for several weeks developed injuries and abnormalities of the kidneys and nerve cells.³

There have been no reported cases of carcinogenicity in humans due to zinc chloride exposure. Except for the ability to induce tumors by intratesticular injections in fowl, no evidence exists that zinc chloride is carcinogenic in animals by oral or intraperitoneal routes of administration.

No evidence examined indicated that zinc chloride is mutagenic.

Basman et al.¹³ demonstrated in animals that HC smoke can be lethal in high concentration or during prolonged periods of exposure because of zinc chloride (Ct of 20,000 mg/min/cu m) and sufficient quantities of cyanogen chloride, phosgene, oxides of nitrogen, hydrogen cyanide, and cyanogen.

HC mixture ingredients and HC smoke products that have been defined and for which concentration limits have been set are summarized in Table 6. Several of these compounds are presumed present in the HC smoke as intermediate products. Additional toxicity data are compiled in Appendix B.

C. Flora.³

1. The toxicity effects of HC smoke clouds on plants and vegetation have not been studied. However, the US Army Medical Research and Development Command Fort Detrick, Maryland, published the results of studies and tests performed on plants contaminated by zinc chloride in 1978.³

2. These results are summarized as follows:

Immersion of leaves of Zea mays L. and Lycopersicon esculentum in zinc chloride solutions caused leaf and plant injury. Zea was more susceptible, the entire plant being involved by day 7. Injury was evident on 75% of Lycopersicon plants within 7 days.

Explants of cauliflower, carrots, lettuce, and potatoes were exposed to 0.0, 0.5, 5.0, or 50.0 mg/l zinc chloride for 20 days. The growth of lettuce and carrot cultures was inhibited at 50.0 mg/l. Cauliflower was very sensitive and could not tolerate more than 0.5 mg/l. The treatment had no effect on potatoes.

Zinc in low concentrations is necessary for the normal growth of plants; however, excess zinc may be toxic to plants. Delayed germination and severely retarded growth was observed in cress and mustard seeds grown in a nutrient solution containing 34-436 mg/l. Concentrations of 3, 5, and 10 mg/l were toxic to orange and mandarin seedlings, flax, and water hyacinths, respectively. A general toxic limit for zinc in plant dry matter is estimated at 400-500 µg/gm.

D. Wildlife and Domestic Animals.³

1. Poultry and pigs exhibit a greater tolerance to dietary zinc than sheep and cattle. Diet composition can influence zinc toxicity in poultry. High zinc levels depressed growth and appetite and induced arthritis and internal hemorrhages in weanling pigs. In sheep, 1000 and 1500 mg/kg of zinc caused reduced weight gains, decreased feed efficiency, and depressed feed consumption. High zinc levels induced tissue changes in sheep and cattle, including subnormal copper levels in the liver, mild anemia, and changes in rumen metabolism. Ingestion of grass containing 500 µg/gm zinc was not toxic to cattle, but higher dietary zinc levels caused an abnormal appetite. Therefore, a general toxic limit for zinc in plant dry matter is estimated at 500 µg/gm.

2. Birds have the tendency to concentrate ingested metals in their eggs and avian embryos are highly sensitive to trace metals. The percent survival of chicken eggs injected with 1 ng/gm to 10.0 mg/kg of zinc chloride ranged from 83% to 9%; a concentration of 50 mg/kg caused 100% mortality. The percent of anomalous animals increased from 2% at a concentration of 0.1 mg/kg to 29% at 10.0 mg/kg. The median tolerance limit of zinc (as zinc chloride) was calculated to be 1.0 mg/kg.

3. Two-way combinations of zinc with either mercury or cadmium exert purely additive effects on chick hatchability. The percent survival of chicks injected

Table 6. Toxicity Summary
Safe Concentrations of HC Reagents and Reaction By-Products

| ISFA ^a | Significant dosages/concentrations ^b | | | | | | | Reference |
|--|---|---|-------------------------------|------------------|---------------------------------------|-------------------------------|-------------------------------|-------------|
| | STEL ^c | TCL ₀ ^d | LCL ₀ ^e | TLV ^f | OSHA ^g TWA ^h | LC ₅₀ ⁱ | LD ₅₀ ^j | |
| Zinc chloride | 2 mg/m ³ | 4800 mg/m ³ for 30 min | — ^k | — (time) | 1 mg/m ³ | — | — | 11,14,16 |
| Perchloroethylene (tetra chloroethylene) | 52 mg/m ³ | 100 ppm | — | — | (670 mg/m ³) | — | — | 11,14,16 |
| Phosgene | — | 25 ppm for 30 min | — | — | 0.4 mg/m ³ 0.1 ppm | 3200 | — | 11,14* |
| Cyanogen | — | 16 ppm | — | 10 ppm | — | — | — | 11,14* |
| Cyanogen chloride | — | 10 ppm | — | — | — | — | — | 11,14* |
| Hydrogen cyanide | — | 120 mg/m ³ per hour or 200 ppm for | — | 10 ppm | — | — | — | 11,14* |
| Hexachloroethane (C ₂ Cl ₆) (unreacted) | 30 mg/m ³ | — | — | — | — | — | 50 mg/kg (human) | 11,14,15,16 |

Airborne zinc chloride can cause death or permanent injury.

May cause reversible/irreversible changes and has been demonstrated as being carcinogenic in mice of both sexes.

Can cause death or permanent injury.

DOT¹ poison, a flammable and highly toxic gas, which can cause death or permanent injury.

Highly toxic and can cause death or permanent injury via oral, dermal, inhalation, intravenous, interperitoneal, and intramuscular routes.

Highly toxic and can cause death or permanent injury via oral, dermal, inhalation, intravenous, interperitoneal, and intramuscular routes.

Has been demonstrated as being carcinogenic for mice of both sexes; can cause death or permanent injury via intravenous routes; can cause reversible/irreversible injury via subcutaneous routes.

Table 6. Toxicity Summary (continued)

| ISFA ^a | Significant dosages/concentrations ^b | | | | | | Comments | Reference | |
|---|---|-------------------------------|-------------------------------|------------------|---------------------------------------|-------------------------------|--------------------|---|-------------------------------|
| | STEL ^c | TCL ₀ ^d | LCL ₀ ^e | TLV ^f | OSHA ^g TWA ^h | LC ₅₀ ⁱ | | | LD ₅₀ ^j |
| Oxides of nitrogen nitrogen monoxide nitrogen dioxide nitrogen oxide | — — — — | — — — — | — — — — | — — — — | — 25 ppm 5 ppm 25 ppm | — — — — | — — — — | Oxides of nitrogen are highly toxic and can cause death or permanent injury via inhalation and contact with skin, eyes, and mucuous membranes | 11,14 |
| Carbon monoxide | — | — | 4,000 ppm for 30 min | — | 35 ppm and 50 ppm | — | — | A toxic and flammable gas which can cause death. | 11,14 |
| Calcium Silicide | — | — | 9600 ppm for 4 hr | — | — | — | — | Effects range from tissue changes that are readily reversible to irreversible changes which do not cause permanent injury or death. Can evolve self-igniting gas (with acids) often igniting spontaneously in the air; can produce a dangerous fire hazard with oxidizers and produce highly toxic fumes. | 14 |
| Aluminum chloride | — | — | — | — | — | — | 3.7 g/kg (rats) | May cause reversible/irreversible changes to exposed tissue but not death or permanent injury. (An intermediate reactant, that reacts with zinc chloride and aluminum oxide.) | 11,14 |
| Aluminum oxide | — | — | 20 MPPCF ^m | — | — | — | — | Common ingredient of soil; at 30 MPPCF even dust would be uncomfortable and irritating. | 11 |
| Zinc oxide | — | — | — | — | — | — | — | Generally of low toxicity, a seed disinfectant, a fungicide trace mineral added to animal feeds. When zinc oxide is heated it evolves a fume of zinc oxide that when inhaled fresh can cause Brass Fanner's Auge or Brass chills (industrial disease). | 11 |

^aISFA - item, substance, force and action of the proposed action considered for evaluation for adverse impact on the environment.

^bAll the significant unit concentrations/dosages are given in the units reported in the literature. All reported amounts per unit time are dosages. Parts per million (ppm) can be converted to mg/m³ by solving:

$$\text{mg/m}^3 - \frac{\text{Molecular Weight of substance} \times \text{ppm}}{22.4 \text{ liters at } 0^\circ\text{C or } 24.5 \text{ liters at } 25^\circ\text{C}}$$

At one atmosphere on 760 mm Hg. This conversion does not take into account the atmospheric or pressure reaction for a gas. This is important if the conversion is made at a higher elevation, Denver for example.

^cSTEL - short term exposure limit, the maximum concentration which workers can be exposed continuously for up to 15 minutes without suffering from irritation.

^dTCL₀ - toxic concentration low for humans (inhalation).

^eLCL₀ - lethal concentration low.

^fTLV - threshold limit value.

^gOSHA - Occupational Safety and Health Act (standard for air).

^hTWA - time weighted average.

ⁱLC₅₀ - lethal concentration for 50% of the population.

^jLD₅₀ - lethal dose for 50% of the population.

^k—No data reported.

^lDOT - Department of Transportation (Recommended standard).

^mMPPCF - million particles per cubic foot.

*McNamara, B. P. Unpublished data. 1971.

with a 1:1 mixture of zinc and cadmium was 78% at a concentration of 1 ng/gm, and 24% at 1.0 mg/kg; 5.0 mg/kg caused 100% mortality. Eighty percent survived treatment with a 1:1 mixture of 1 ng/gm zinc and mercury, and 8% with 10.0 mg/kg.

E. Aquatic.³

1. Zinc Chloride (ZnCl_2).

The aquatic toxicity of zinc chloride and zinc ions to fish is presented in Appendix B. In soft water (hardness between 20-30 ppm as CaCO_3), zinc has 96-hour LC_{50} values near 0.1 mg/l. In hard water (200-300 ppm hardness as CaCO_3), the toxicity is between 1-10 mg/l. This median lethal concentration will vary depending on the size of the exposed fish.

EPA water quality criteria to protect freshwater aquatic life for zinc is related to hardness. At hardnesses of 50, 100, and 200 ppm as CaCO_3 , the recoverable zinc should not exceed 180, 320, and 570 $\mu\text{g/l}$ at any time (Federal Register/Vol 45 (231) Nov 28, 1980. 79341).

2. Hexachloroethane C_2Cl_6 .

For protection of freshwater aquatic life, the EPA has proposed a 24-hour average hexachloroethane concentration of 62 $\mu\text{g/l}$, not to exceed 140 $\mu\text{g/l}$ at any time; for saltwater aquatic life, the 24-hour criterion would be 7 $\mu\text{g/l}$, not to exceed 16 $\mu\text{g/l}$ at any time.

V. ENVIRONMENTAL IMPACTS OF HC SMOKE

A. Research and Development.

Research and development of HC smoke munitions has been discontinued because of the concern about health effects.

The Chemical Research and Development Center, under the direction of the Project Manager for Smoke/Obscurants, is conducting a product improvement program (PIP) to replace HC smoke mixes with a less toxic red phosphorus (RP) pyrotechnic mix. The PIP began in November of 1979 with an Ad Hoc Working Group and the target year for replacement of HC with RP is 1985. This program is discussed in the Programmatic Environmental Assessment for Red, White, and Plasticized White Phosphorus and the Life Cycle Environmental Assessment, PIP No. DA1-80-09-7302 and DA1-82-09-7301, "Development and Production of Red Phosphorus Based Smoke Agents for AN-M8 Grenade" and "ABC M5/M4A2 Smoke Pots."

Described below are the actions ongoing to replace the HC mix in future scheduled production of the M8 Smoke Hand Grenade and the M5/M4A2 Smoke Pots. Medical research is being conducted to determine whether the replacement RP mix is less hazardous to industrial/troop personnel and the environment.

This action plan excludes the M84A1 105-mm Cartridge and the M116A1, 155-mm Projectile. No future production is scheduled for the M84A1. The M116A1 is presently completing production life-cycle and will be replaced by future productions of the XM825 155-mm Projectile which has a WP fill.

B. Manufacturing and Production.

Hexachloroethane (C_2Cl_6) is not currently manufactured in the US, and any future manufacture here is doubtful. All military and civilian supplies are imported from France, Spain, and Japan. HC smoke mixers are formulated from purchased materials and loaded into grenades or canisters at Pine Bluff Arsenal (PBA), Pine Bluff, Arkansas.

The mission of PBA includes receipt, storage, surveillance, renovation, shipment, and demilitarization of pyrotechnic devices and their components. It also has a load, assembly, and pack (LAP) mission for specific items. The production of white smoke is the major use of hexachloroethane by the military. Production discharges of the HC mix are controlled by pollution abatement facilities. The main entry of this chemical into the environment from civilian use would be from the production of fluorocarbons used in dry cleaning solvents, fire extinguishers, refrigerators, aerosols, and food propellants.³

1. Alternatives Considered.

The alternatives to be considered include: (a) continue manufacturing HC smoke at PBA until a suitable replacement is developed and accepted; (b) replace HC smoke with a red phosphorous mix; (c) stop HC smoke production; or (d) take no action (continued use without product improvement).

2. Environmental Impacts of Activities.

a. Continue manufacturing HC smoke.

Since the necessary facilities, procedures, and safety equipment to assure HC containment and to preclude environmental contamination presently exist at PBA, it is desirable from safety and cost aspects that mixing the HC formulation for grenades and canisters should continue. The production should continue for training and testing purposes until 1985, at which time all HC production would be switched to the approved alternate mix. The manufacturing risks associated with hexachloroethane (C_2Cl_6) at PBA are detailed in a special study prepared by the Army Environmental Hygiene Agency (AEHA).¹⁷

The major problems with HC mix during production are the dusts created and their association to working personnel, the risk of accidental fire/fumes associated with a hot/humid environment, and the risk of dust explosion in an enclosed area. When heated to decomposition HC emits highly toxic fumes of phosgene. To ensure that the dust in the air during processing is kept to the lowest possible level, a "closed filtration system" is used for formulating HC mixes while controlling dust. Electric vacuum cleaners insure clean and safe working conditions. Standard operating procedures ensure that explosive proof tools are used and that correct storage and transport regulations are observed. The recommended 8-hour Occupational Safety and Health Administration (OSHA) federal standard for hexachloroethane in the workplace is 1 ppm (9.7) mg/m³ with a notation on skin. This notation refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes.

Discharges of wastes into the waterways are controlled by permits from the National Pollutant Discharge Elimination System (NPDES).

b. Replace HC smoke with red phosphorous mix immediately.

The proposed Medical Evaluation Program (MEP) to evaluate RP will not be completed until the latter part of 1984. Provided evaluations go well and approval to use is received, then the replacement program may be implemented in 1985, but even then it will take time to build up a stockpile for the replacement mix.

c. Stop production of HC smoke.

(1) Stopping production of HC without a replacement would deprive the Army of this white smoke capability and also deplete its screening capability on water (floating pots). Thus, this alternative would be inconsistent with current requirements for national security.

d. No action.

Continued use of HC without product improvement would be contrary to directed action to eliminate safety hazards from the inventory of HC munitions by replacement with tested, less toxic, noncarcinogenic chemicals.

3. Recommended Mitigation.

Current mitigation measures are adequate. All production of HC mixes are controlled by a closed system, a vacuum system to adequately clean up spills and dust, an incinerator scrubber system to collect and control airborne emissions, and a separate slurry/waste operation to dispose of collected wastes. All operations are in compliance with federal, state, and local environmental laws and regulations.

Should emergency situations dictate handling or working around hexachloroethane where all the above controls are not available, then general handling procedures should include wearing thick working gloves, safety goggles, and the universal gas mask. Appropriate clothing and equipment to prevent prolonged or repeated skin contact should be used, and workers should wash promptly with soap and water when skin becomes contaminated.

C. Training and Testing.

1. Overview/Discussion.

The Army has recently experienced a substantial revival of interest in using smoke to protect troops and installations and to support tactical maneuvers. The US Army Chemical School located at Fort McClellan, Alabama, resumed training of personnel to support this program in 1980. This training provides experience in theory, generator operations, and practical application under field conditions.

Since training and testing occur in much the same type of environment and, in many cases, ranges serve both purposes, the impacts addressed below will be considered applicable to both situations unless specifically noted otherwise.

HC smokes are used at Army installation training areas. In 1981 TRADOC installations detonated 125,000 HC munitions, and over 27 tons of residuals were estimated to be released on/over smoke ranges.

Training areas may be located adjacent to fishing ponds, hunting areas, areas leased for grazing beef and milk cattle, or off-post housing areas and cantonment areas. Although the toxicity of each of the individual compounds is known, little is known about the fate of these compounds under deployment circumstances and the possible synergistic or antagonistic effects on living organisms under such intermixing conditions. Studies and concluding documentation are scheduled for release during FY83 concerning these data gaps.

HC white smoke continues to be important for utilization in testing and training exercises to demonstrate white smoke capabilities.

2. Alternatives Considered.

The alternatives to be considered include: (a) continue deployment of HC smoke; (b) develop new smoke mixtures; (c) take no action; and (d) reduce or modify training/testing.

3. Environmental Impacts of Alternatives.

Continued deployment of HC smoke in pots and grenades are included in the following discussions. The use of HC mix in 105-mm and 155-mm munitions will not be addressed here since HC utilization in these munitions is no longer included in modern combat scenarios.

As HC smoke mixture burns, intense heat and smoke are produced, with approximately 80% by weight of the aerosol smoke being zinc chloride and 20% other by-products.

Research established that the zinc chloride and lesser amounts of other toxic by-products in concentrated HC smoke, located near functioning HC smoke pots/grenades and generators, especially in enclosed spaces, can cause casualties.^{8,18}

Because of concern about the individual or combined effects of other by-products in the generation of HC smoke, a comparison was made with zinc chloride to determine the adequacy of the calculation for downwind hazard/safety distance for zinc chloride to include all of the other toxic products of HC smoke (Table 7).

Sixty-eight of individual/combined other toxic product(s) (excluding zinc chloride) would be required to produce the same downwind hazard/safety zone as that produced by zinc chloride alone.⁸ Present information about the negligible amounts produced by other toxic products indicates that the downwind hazard safety zones established for zinc chloride should allow dissipation of other potential individual and total toxic airborne materials to a safe level during each HC smoke dissemination trial of the proposed action.

The environmental effects for zinc chloride depend upon the quantities dispersed and the spacing of the smoke generators (usually 70 meters apart), the frequency of the smoke-generating operations, and the environmental and meteorological conditions at a particular site. In general, the lighter the winds, the more stable the atmosphere; the absence of plume rise will contribute to higher concentrations and longer distances for downwind hazard. To illustrate this point, sample calculations of downwind distances were made for an M5 smoke pot released at night and during the

day. It is assumed that the 13.622 kg of HC mixture produces 10.625 kg of zinc chloride. The meteorological inputs used were 1 mps wind speed and F. Pasquill stability for night, and 1 mps wind speed and D. Pasquill stability for day.* Calculations were made without and with plume rise, the latter using heat of combustion of 490 cal/gm of HC mixture over a 12-minute burn time. Calculations were made for a peak centerline concentration of 2 mg/m^3 and for three total dosages of 20, 2000, and 4800 mg/m^3 (STEL through TCL Low). Table 7 shows the results of these calculations.**

After deposition of zinc chloride on soils, its migration or mobilization would be governed by many factors. Before these are discussed, it is imperative to point out that the soils themselves contribute to various concentrations of zinc; background levels range between 10-300 mg/kg.

For night release, note the drop in distance for peak centerline concentration when the wind speed is increased from 1 mps to 3 mps, and the slight decrease with plume rise. Similar decreases also occur with total dosages. Also, dosage levels of 2000 and 4800 mg-min/m^3 do not occur at the surface with plume rise, except immediately downwind from the source. The day release is during neutral stability, which is less stable and permits faster cloud growth in the vertical; greater plume rise is unimpeded. The higher plume rise (95 m) occurs with 1 mps wind speed and the lower plume rise (50 m) occurs with 6.5 mps wind speed.**

The distances shown with and without plume rise, for either day or night, are the most probable ranges for the given set of meteorological conditions. The actual distance that occurs will most likely fall between these ranges. Because there are so many interacting factors involved that can vary the concentration or dosage downwind, calculations for hazard/safety using actual conditions should be made anytime a potential hazard exists.**

Depending upon the location and surrounding environment of the site of smoke generating operations, zinc chloride would be expected to settle down to the ground, plants, vegetation, and waters, the ground being the main target. In the worst case, the ground (soil surface) in the immediate vicinity of the generators may be contaminated with zinc chloride. There are only 6356 gm of zinc oxide in the HC mixture of 13.6 kg, of which 80% or 5106 gm are zinc. The concentrations will rapidly be exceeded at a given site if the smoke generating operations are continued.³

Zinc chloride in the presence of moisture will occur as zinc ion. The factors which influence the mobility of zinc ions in soils are: hydrogen ion activity (pH),

*The dispersion of atmospheric pollutants is an important factor in describing an environmental setting. Such dispersions are governed by environmental regulations which impose air-quality standards. In meeting these standards, the capability of the atmosphere for dilution of materials must be considered. A stability classification system for dispersion capability has been developed by Pasquill.¹⁸ Stability category A is very unstable and stability category F is very stable (affording the least dilution). Categories C and D describe neutral stability.

**Rengers, E., Dugway Proving Ground, UT, personal communications.

Table 7. Downwind Hazard/Safety Distances*
 1 each M5 Smoke Pot (HC)
 (13.622 kg - fill wt, 10.625 kg - $ZnCl_2$)
 (12-minute release)

| NO PLUME RISE Exposure Level (Wind Speed) | PLUME RISE (meters) | | |
|--|---------------------|-------|-------------------------|
| | 1 mps | 3 mps | 1 mps |
| | NIGHT (F Stability) | | (18 m Plume Rise) |
| 2 mg/m ³ peak concentration | 2900 | 2000 | 3600 |
| 30 mg-min/m ³ total dosage | 3700 | 1720 | 3200 |
| 2000 mg-min/m ³ total dosage | 190 | 80 | - |
| 4800 mg-min/m ³ total dosage | 100 | 40 | - |
| | DAY (D Stability) | | (50 to 95 m Plume Rise) |
| 2 mg/m ³ peak concentration | 1100 | | - |
| 30 mg-min/m ³ total dosage | 950 | | - |
| 2000 mg-min/m ³ total dosage | 80 | | - |
| 4800 mg-min/m ³ total dosage | 50 | | - |

*Rengers, E., Dugway Proving Ground, UT, personal communication.

particle size distribution, pore size distribution, presence of lime in soils, presence of hydrogen oxides, climate, and degree of oxygenation.³

The mobility of zinc in acidic soils is greater than in neutral or alkaline soils. Movement of zinc to 30 cm has been observed in an acid soil which had received a surface application of 16.3 metric tons/ha of sewage sludge. Practically all of the zinc remained in the surface 20 cm of soil for 12 years following application of 84 metric tons/ha of sewage sludge. There are also data showing evidence of movement of zinc below 15 cm in soil over a 3-year period after application of 44-166 metric tons/ha of sludge. Further leaching and/or runoff of zinc into streams or water supplies will depend on the quantity of rainfall and the level of the water table at the site.

Fallout of zinc chloride from the smoke on flowing rivers and streams normally will not pose any problem, but may vary based on stream/river size, flow rate depth, location, tidal/nontidal characteristics, etc. However, fallout can and will accumulate in still waters such as ponds and lakes.³

Since actual estimates of the quantities of zinc chloride released in the environment from smoke-generating operations are not available, approximate concentrations have to be employed in an attempt to evaluate the impact of zinc chloride by comparison with known effective levels. Following is a synopsis of the known effects of zinc chloride which could be encountered by repeated generation of the smoke.³

a. Effects on Humans.

The lethal dose of zinc chloride smoke is not known, but has been estimated as 50,000 mg/min/m³. Such concentrations are not likely to be encountered under ordinary field exercise conditions. In a closed room of 3 m³, however, this concentration can be achieved by one smoke pot in 2-3 minutes.

b. Effect on Domestic Water Supply.

The 1962 drinking water standards of the US Public Health Service set a limit of 5 mg/l of zinc as acceptable in water supplies. The World Health Organization and European standards are similar. The normal human intake of zinc is estimated at 10-15 mg per day. Very high concentrations of zinc in water can be toxic, a concentration of 675-2280 mg/l zinc (as zinc sulfate) has been found to be emetic.

c. Effects on Plants.

While low concentrations of zinc are a nutritional requirement in most crops, high concentrations may be toxic. Concentrations of 3 mg/l of zinc in nutrient solutions have been found to be toxic to orange and mandarin seedlings, 5 mg/l is toxic to flax, and 10 mg/l is toxic to water hyacinths. Zinc sulfate at levels of 25-100 mg/l has been found to be toxic to oats. Concentrations of 6.5 mg/gm zinc in soils considerably reduce the yield of grass.

During an observation period of 18 days, 54-436 mg/l of zinc in nutrient solutions delayed germination and greatly retarded the growth of cress and mustard seeds in solution culture.

From the estimates of the amount of zinc chloride released from one or two HC smoke pots, it appears that phytotoxic concentrations may not be produced in the environment from occasional use. However, toxic levels may be reached if frequent and continuous smoke-generating operations are involved at the same site.

d. Effects on Aquatic Organisms.

Zinc can enter waters directly as fallout from zinc chloride smoke, leaching from soils, or runoff. Leaching may not be a problem if the soil is neutral or alkaline, since zinc is not readily mobile in these soils. When the soil is acidic, zinc may leach into the water supplies. Fallout of zinc chloride on flowing waters such as rivers and streams should not be hazardous since toxic concentrations will not normally be accumulated in these sources. Some problems may be encountered in the case of still waters, such as ponds, where continuous generation of the smoke at one site may increase the levels to toxic limits. The exact amount of zinc chloride contamination will depend upon the nature, frequency, and location of the operations.

e. Effects on Domestic Animals and Wildlife.

Zinc has been recognized as an important dietary element for humans as well as animals. The lack of trace amounts of zinc in the diet can produce various disease syndromes. Therefore, the physiological effects of zinc must be considered on the basis of whether the disease syndrome is produced by an excess or a lack of zinc in the diet.

Zinc chloride generated as a result of smoke-producing operations becomes accessible to domestic animals and wildlife through fallout on water and grazing areas. Grasses, forage plants, and other vegetation can accumulate zinc, either as a result of direct fallout or through absorption from the soils.

The toxic levels of zinc chloride in the grazing areas and in drinking waters would be attained only if the same grounds were used repeatedly for smoke-generating operations. Remember that in calculating toxic concentrations, soil background levels of 10-200 mg/kg of zinc have been documented.

f. Effects on Natural Populations.

Testing and training sites can be adequately cleared of non-essential personnel and domestic animals by timely posting, notification, and monitoring.

g. Effects From Noise.

Noise is not considered a problem with smoke pots or grenades. Should projectiles be reinstated, then noise will be generated at the muzzle of the gun, from the shock wave of the projectile in flight, and at the impact area from the functioning of the munition. The degree to which the noise affects humans and animals depends upon numerous factors, including location, frequency of firing, meteorological conditions, etc.

h. Effects From Wastes and/or Spills.

The wastes generated will consist mostly of test or training debris, i.e., expended rounds/pots and/or packaging materials or munition duds. SOPs and test procedures will insure that all debris is collected and Technical Escort Detachment personnel will dispose of duds. The Installation Spill Contingency Plans shall address the containment and clean up of spills.

i. Effects on Air Quality.

Impacts on air quality are subject to state and local laws and regulations; however, since smoke testing is usually conducted in remote areas of various installations, limited cloud cover may transcend small installation boundaries. Every effort should be made to consider weather conditions and seek support in predicting or utilizing downwind hazard predictions for the area. If any of the aerosol cloud was to encroach on local communities, it would be expected to be of such low grade that effects would be negligible.

(1) Develop New (Replacement) Smoke Mix.

Red Phosphorus mix is the proposed alternative for HC smoke in grenades and smoke pots.

Environmental impacts and proposed actions associated with RP have been discussed in earlier reports.^{19,20}

(2) Stop Deployment of HC Smoke.

This alternative would eliminate all direct environmental impacts associated with training or testing, but is unacceptable in view of current requirements for national security.

(3) No Action.

Continued deployment of HC smoke without product improvement would be contrary to directed action to eliminate safety hazards from HC munitions.

(4) Reduced or Modified Training/Testing Alternative.

Indoor smoke training would eliminate certain environmental risks associated with field training, but at the expense of creating other environmental impacts while preparing structures to house such training. Impacts of outdoor smoke training are not sufficient to justify expenditures for indoor training of the various smoke-generating systems. Additionally, reduction in training requirements would be unacceptable in view of current requirements for national security.

4. Recommended Mitigation.

a. Appropriate weather conditions shall be selected which will confine the smoke cloud to the military reservation. Weather conditions should be monitored before and during open air burning of HC smoke to avoid undesirable downwind travel.

b. The Post chemical officer, or a designated person in Range Control, should receive notification of smoke use in order to assure dispersion over time and space. When a pattern of excessive usage appears, coordination with the unit commander should be sufficient to resolve it. Areas and conditions for potential use should be precisely stated in range regulations, and the areas should be as large as possible to reduce concentrations. Areas of heavy use should be monitored periodically for vegetation or other environmental change. Regulations and training should also address the matters of proper munition or generator use to prevent contamination from improper usage and fire damage from burning munitions.²¹

c. Before deployment of HC munitions, Range Control will coordinate with or notify appropriate Air Pollution Control Authority, Post Fire Department, Post Forester airfield control tower, and other appropriate specified agencies. Road guards should be provided as necessary during unit training to provide warning of cloud limits along military-use roads. There should be some ground or air monitoring with positive communication between headquarters and operators of the smoke generator to physically track the downwind edge of the cloud and observe if the cloud is drifting near the reservation boundary or a commercial highway.

d. Individuals with respiratory conditions, including asthma, cardiac conditions, severe facial acne, or any active dermatitis should be evaluated by a medical officer before being allowed to participate in smoke field training. Commanders must ensure that in testing and training, exposures to HC smoke should be controlled in accordance with the occupational and environmental exposure guidance established through The Surgeon General as command policy.*** "There are no specific known cases of physical impairment associated with smoke training. There is, however, similarity between the potential effects of current smoke agents and other known causes of physical disability associated with exposure aerosols. It is, therefore, prudent to take reasonable precautions in exposing personnel to field concentrations of smoke and to insure that respiratory protection (protective mask) is readily available." These guidelines as they pertain to HC smoke are summarized as follows:

(1) Personnel will carry the protective mask when participating in exercises which include the use of smoke.***

(2) Personnel will mask when exposed to any concentration of HC smoke.***

(3) Bathing and laundering of clothing following exercises will eliminate the risk of skin irritations after exposure to HC smoke.

(4) Personnel handling HC mixes or smoke munitions must take precautions to avoid contaminating exposed skin. If eyes, skin, or mucous membranes are contaminated, prolonged irrigation with water should be immediately. Prompt medical attention should then be sought. An appropriate alternate to the deluge of water is a 15-minute irrigation with neutral 0.05M EDTA solution, but again application of a chelator (EDTA) should not be attempted unless trained medical personnel are present. Emergency deluge water, if used, should be applied at a rate of 1.5 to 2 gpm for 20 to 30 minutes. This means a sufficient quantity of deluge water should be on site. All contaminated clothing should be removed, and the patient should be placed in a deluge-type shower as quickly as possible if the contaminated area is large. To decrease the risk of zinc chloride burns, skin abrasions should be adequately protected, and minor injuries to the hands and forearms should receive prompt treatment.

(5) Special care must be taken when using HC smoke to insure that appropriate protection is provided to all personnel who are likely to be exposed. When planning the use of HC smoke in training, specific consideration must be given to weather conditions and the potential downwind effects of the smoke. Positive controls (observation, control points, communications) must be established to prevent exposure of unprotected personnel.

*Letter, DRSTE-ST, TECOM, 25 March 1981, subject: "Health Hazards-Chemical Smoke Munitions Usage and Demilitarization."

**Messages, DAMO-SSC, subject: Smoke Safety, dated 281255Z Jul 78; DAMO-SCC, subject: Smoke Safety, dated 052005Z Sep 78, and DAMO-NNC, subject: Safety Considerations for Use of HC Smoke During Training, dated 211549Z Feb 80.

(6) Publications should be reviewed to ensure that appropriate safety precautions for HC smoke are included in training and employment guidance.

(7) Females may participate in training exercises involving HC smoke subject to all above guidelines and masking provisions.***

e. Smoke training/testing areas will be located so as to avoid the nesting areas of endangered wildlife.

f. Smoke and noise from these operations may disturb wildlife, particularly the migratory duck and geese populations. It is expected that some shifting in roosting and nesting patterns will take place within local areas; however, no significant reduction in wildlife population would be likely.

g. When preparing deployment scenarios, test/training coordinators should evaluate the following measures as a checklist against downwind hazards.

(1) The proposed action should not extend beyond installation boundaries or exceed prescribed regulations.

(2) Calculate the amount of substances necessary to produce the "no effects" concentrations and predict associated downwind hazard distances.

(3) The downwind hazard zone should not include any installation area containing nontest and/or nontraining personnel.

(4) Domestic animals should be absent from the downwind hazard zone.

D. Transportation and Storage.

1. Transportation.

As indicated under the manufacturing section, there are no longer any US manufacturers of hexachloroethane (C_2Cl_6). All hexachloroethane used in the US is imported from France by Rhodia, Inc. It is shipped to PBA where the HC smoke mix is formulated and loaded into grenades and smoke pots for temporary storage awaiting shipment to army installations. The transportation and storage classifications and regulations are as indicated under Section III.F of this document.

*Letter, DRSTE-ST, TECOM, 25 March 1981, subject: "Health Hazards-Chemical Smoke Munitions Usage and Demilitarization."

**Messages, DAMO-SSC, subject: Smoke Safety, dated 281255Z Jul 78; DAMO-SCC, subject: Smoke Safety, dated 052005Z Sep 78; and DAMO-NNC, subject: Safety Considerations for Use of HC Smoke During Training, dated 211549Z Feb 80.

Impacts of Transportation.

If hexachloroethane (C_2Cl_6) is spilled or leakage occurs, it could affect the body if inhaled, if in contact with the eyes or skin, or if it is swallowed. It may also be absorbed through the skin. Exposure to hot fumes may cause irritation of the eyes. In the event of an emergency, institute first aid procedures and send for medical assistance.

Spill and Disposal Procedures (NIOSH Guidelines)

Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed. If hexachloroethane is spilled, the following steps should be taken: (a) Ventilate area of spill. (b) Collect spilled material in the most convenient and safe manner for reclamation or for disposal. Liquid containing hexachloroethane should be absorbed in vermiculite, dry sand, earth, or a similar material. (c) For waste disposal, product residues and sorbent media may be packaged in epoxy-lined drums and disposed of at an EPA-approved disposal site. If over 1000 kg, waste must be disposed of subject to RCRA regulations for disposal of hazardous waste. If less than 1000 kg, they may be disposed of in a facility defined by RCRA for hazardous waste management that has a permit or interim status, or in a permitted municipal or industrial solid waste facility. See Title 40, CFR 261.5 and 261.33. Destruction by incineration at high temperatures with scrubbing equipment (reference TN 9-1300-277 for approved facilities). Confirm disposal procedures with environmental engineers and regulatory officials. (d) To extinguish small fires, dry chemical, CO_2 , should be used. Water spray or foam should be used for large fires (deluge of water spray, fog, or foam).²²

CAUTION: HC mix reacts with water or salt water; therefore, should leakage occur in the vicinity of fresh or salt water, it can start burning with toxic effects to local personnel or the environment, especially in confined quarters. If a fire should occur, it must be deluged with water because small volumes of water are ineffective and may increase the fire.

2. Storage.

Storage classifications and requirements are included in Section III.G.

Impacts of Storage.

Hazards and/or area contamination from leakage or fire while in storage will produce the same type impacts indicated for transportation. Therefore, procedures in the "Spill Prevention Control and Countermeasure Plan" or the Guideline procedures of the National Institute for Occupational Safety and Health (NIOSH) listed in paragraph D.1.a. above should be followed.

E. Demilitarization/Disposal.

"General Instructions for Demilitarization/Disposal of Conventional Munitions" which includes HC smoke is contained in TM 9-1300-277, dated March 1982. The manual provides references to sources of information, regulations, and technical expertise for the purpose of ensuring that demilitarization/disposal activities utilize and implement the latest guidance and technical knowledge.

As a result of a serious incident in which a cloud drifted off-post during demilitarization of M5 Smoke Pots at Lexington-Blue Grass Depot, the following occupational and environmental guidance was established and distributed from The Surgeon General as command policy. In disposal of HC smoke, no open burning should be allowed. If other disposal options are undertaken, exposures of involved personnel to the components of HC smoke or disposal by-product should be maintained below permissible exposure limits established for those components or by-products in 29 CFR 1910.1000.

Hazardous Waste Consideration.

Hexachloroethane phosgene, carbon tetrachloride, and hexachlorobenzene qualify and are listed as hazardous wastes under RCRA and are also listed as a toxic wastes under numerous state regulations. In addition HC mix from malfunctioning/damaged munitions and munitions declared excess (for disposal) must be accounted for as toxic waste.³

1. Alternatives Considered.

Demilitarization/disposal procedures that are approved alternatives for implementation during the various life cycle phases of hexachloroethane, HC smoke mix, and/or HC munitions include (a) open burning, (b) incineration, (c) Explosive Ordnance Demolitions (EOD) for subsequent disposal, and (d) storage for subsequent disposal by the Defense Property Disposal Office (DPDO).

When demilitarization prior to disposal is a requirement for HC munitions it shall be conducted in accordance with the provisions of the Defense Demilitarization Manual, DOD 4160. 21-M-1, July 1979.

a. Open Burning.

DARCOM Supplement 1 to AR 200-1, Chapter 4, para 4-4f, states that the open burning of HC, WP, and colored smoke is prohibited. Requests for exception to this policy should be forwarded to Commander, DARCOM, ATTN: DRCSG, with appropriate justification.

b. EOD Disposal.

Loose HC mix and munitions containing HC mixes that have malfunctioned/been damaged/declared excess and that can be collected will be disposed of by EOD personnel for disposal. This procedure is especially applicable to test sites.

If a safety (handling) hazard exists with HC munitions and for excess HC mix, the hazardous material may be demilitarized in place according to approved procedures. However, disposal operations should be conducted only at permitted hazardous waste facilities. The after-action report will provide the Environmental Quality Coordinator with a record of the burial showing the date of the action, the item or material buried, the number of items or weight of material buried, the approximate location of the burial, and confirmation that the hazardous waste was immediately covered with soil.

c. Incineration.

Disposal by incineration is encouraged where approved incinerators exist and emission limits are monitored for compliance with state and federal requirements. Such incinerators exist where the smoke is collected and washed in scrubbing towers; the scrubbing water is then treated to conform to local requirements and NPDES permits. See reference TM 9-1300-277 for existing incineration facilities.

d. DPDO Storage.

Storage of HC waste at an installation must comply with the procedures outlined in DOD 4160.21-M-1 and AR 200-1 while awaiting final demilitarization/disposition actions.

2. Environmental Impacts of Activities.

Environmental risks associated with demilitarization and disposal procedures of smoke-generating hardware should be minimal. Any emissions and effluents that may result from demilitarization/disposal, including incineration, must be maintained within the limits set forth by EPA, local, and state air quality standards. Controls are enforced through air quality standards, National Pollution Elimination Discharge System (NPDES), and RCRA requirements. All HC waste remaining after demilitarization must be disposed of at controlled facilities or else disposal actions could result in potentially adverse environmental impacts.

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VII. CONCLUSIONS

1. It is a recognized fact that HC smoke mix and its combustion products may pose health hazards to manufacturing personnel and troops during training and testing exercises as detailed in the toxicological section of this report. Therefore, until HC smoke can be replaced by an approved substitute mix, controlled use of HC smoke should be enforced. Controlled use means adherence to safety aspects and regulations and the use of suggested mitigation to minimize adverse impacts to the quality of the human environment.

2. The following mitigating controls should be included along with the continued use of inventory HC stocks: (a) enforce the Army directive to mask in the presence of HC smoke; (b) closely regulate the deployment of HC smoke on all its installations; (c) restrict HC deployment to areas of the installation as far as practically possible from cantonments and other populated areas; (d) take special precautions to protect higher risk individuals such as those highly allergic, children, and the aged and; (e) under no conditions should HC be deployed indoors or in confined quarters.

3. A study is presently underway to determine: (a) the exposure that a soldier may experience when HC smoke is deployed during conventional smoke exercises; (b) the effects of HC on selected environmental organisms; and (c) an estimate of the potential health effects to the population at risk. When these results are released, an update of this document will be prepared, if required, to reflect all pertinent findings.

4. It is recommended that the PIP program to select a suitable less toxic substitute for HC smoke be continued.

5. Additional information is needed in the following areas for HC smoke munitions:

a. Identification and quantification (percentages) of the combustion products of HC smoke

b. Measurement of deposition rates of these combustion products

c. Data on the toxicology and environmental fate of the mix compounds and reaction by-products in combination with each other under actual deployment and also the synergistic and antagonistic effects on living organisms.

6. Although the effects on the environment resulting from exposures to HC smoke and its compounds, or the fate of these compounds in the environment, are not fully documented at this time, the potential for adverse impact on populations and animals in the smoke area is not considered significant. HC screening smokes have been tested on various army installations for several years without adverse impact, and with continued alert control, future adverse impact is not anticipated. An Environmental Impact Statement is not required and a Finding of No Significant Impact will be published.

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APPENDIX A
CLIMATIC & GEOLOGICAL FACTORS ON SMOKE CLOUDS

The effects of weather, particularly wind speed and direction, and terrain conditions are important factors to be considered in smoke scenarios. The movement of smoke depends upon the speed and direction of the wind. Wind direction and velocities are important in estimating the amount of smoke required and the effects produced. Another factor is: atmospheric stability - temperature, humidity, precipitation, and cloud cover.

It is hoped that the following information will be helpful in preparing smoke scenarios and in calculating hazard distances for training and testing.*

1. Winds.

Transport (steering) winds have the greatest influence on smoke operations. Transport of the smoke plume from a surface source may occur in one or more layers extending several hundred meters above the surface. Heat is released when smoke is produced and the heat may cause some of the smoke plume to rise to higher levels. Accurate estimates of transport winds require measurements in these layers.

The movement of smoke depends on the speed and direction of the wind. These factors are important in determining the number of smoke-producing sources needed and the requirements for munitions for a given smoke operation. Placement of smoke varies with windspeed. Difficulties are encountered with smoke generators if windspeed is outside the desired range (4-10 knots). HC smoke tends to rise when the wind is less than 4 knots and is torn apart by winds greater than 13 knots. Additional generators may be required to establish and maintain a screen at higher windspeeds. Windspeed also has a major influence on persistence and duration of a screen, as well as on the distance of travel.

Appropriate placement of smoke sources varies depending on the wind direction encountered in the target area (Figure A-1). Source spacing for an area screen should be such that merging of plumes occurs prior to reaching the area to be screened. The baseline on which the sources are to be placed may be fixed by circumstances; ideally, it will be sited to suit the type of smoke source most efficient for the purpose.

*Data included in this appendix was gathered from the following sources:

Smoke, An Obscuration Primer. Joint Technical Coordinating Group for Munition Effectiveness. 61 JTCG/ME-77-13. 13 March 1978. UNCLASSIFIED Publication.¹

Rengers, Edward. Dugway Proving Ground, UT. Personal communications. May 1983.²

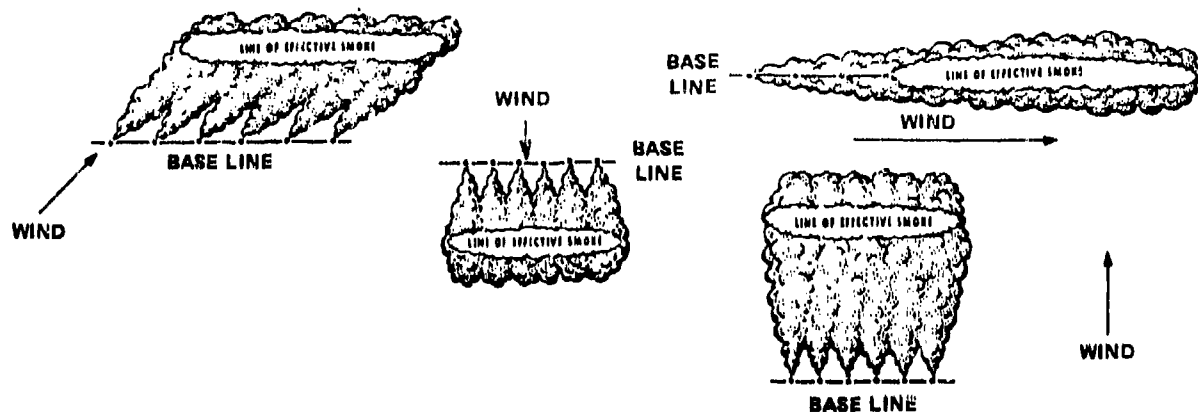


Figure A-1. Effect of Prevailing Wind Direction

The point at which smoke is placed is important. The smoke should be placed upwind so that it obscures the vision of the enemy along the maneuver-target line. Under normal circumstances this point should be about 100 meters short on the maneuver-target line and 100 meters upwind of the enemy location. Care must be used with headwinds, since the smoke may be blown onto the maneuvering element. With a tailwind, smoke should be placed at least 200 meters short of the target to preclude the smoke from landing beyond the target.

2. Atmospheric Stability - Temperature.

The rate of vertical spread from a source on a stationary surface depends on air stability. In unstable air, smoke will rise more quickly than in stable air. Conditions of atmospheric stability that are of interest are inversion, neutral, and lapse; these result from temperature differences of the air from the surface upward. From these gradients, it can be predicted whether a smoke cloud will remain at a constant altitude (inversion), rise at a moderate rate (neutral), or rise rapidly (lapse). The effect of temperature on smoke is slight. The only effect is the relationship of temperature to relative humidity and a warming of the smoke cloud due to solar radiation.

(a) Land Inversion.

An inversion exists when there is an increase in air temperature with an increase in height above the ground. During an inversion, smoke spreads and diffuses slowly. These conditions are favorable for production of a smoke haze or area screen (Figure A-2) and occur on clear calm nights.

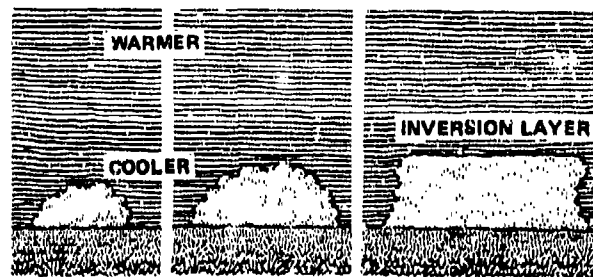


Figure A-2. Development of Smoke Cloud - Inversion

(b) Land Neutral.

Neutral conditions have characteristics between lapse and inversion, since no temperature gradient exists. Neutral tending toward lapse is favorable for smoke curtains; neutral tending toward inversion is favorable for area screens (Figure A-3). These conditions occur an hour or so before and after sunrise and sunset.

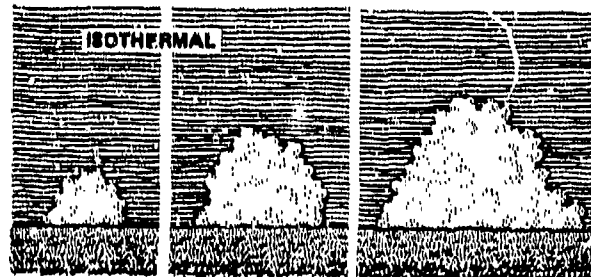


Figure A-3. Development of Smoke Cloud - Neutral

(c) Land Lapse. A lapse condition exists when there is a decrease in air temperature with an increase in height above the ground. The air is unstable, with much air turbulence; smoke tends to rise and diffuse rapidly (Figure A-4). The lapse condition is favorable for production of smoke curtains and is least favorable for smoke screens. It occurs on clear days when winds are light.

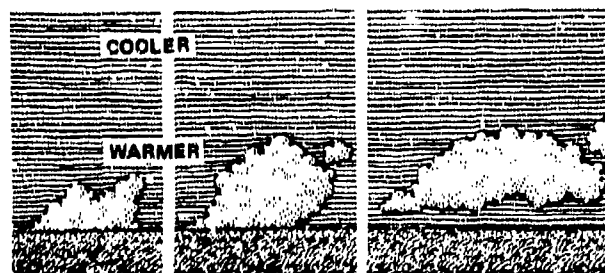


Figure A-4. Development of Smoke Cloud - Lapse

(d) Air-Sea Effects.

An inversion over water occurs more frequently during the day than at night since the air above the water surface can be heated or cooled more rapidly than the water. In general, if the water temperature is the same as, or lower than, the air temperature, an inversion will result. Neutral conditions result when the air temperature is within one degree of the temperature of the water. When the water temperature is more than one degree warmer than the air, a lapse will result.

(e) The Land-Air Interface.

In the evening and night, following the earth's cooling, there is a rapid cooling of the air close to the surface. The most stable condition is developed when the heavier, cooler air is beneath a warmer layer. Over land, a lapse is most probable on clear summer days, from about 2 hours after sunrise to about 2 hours before sunset. This results in an onshore breeze during the day and, at night, warm air rising from the water results in offshore breezes.

3. Humidity.

HC smoke particles absorb moisture and increase in size, thereby increasing their density and making the smoke more effective. HC smoke munitions produce a denser smoke when the humidity is high than when it is low. High humidity is a favorable employment condition.

4. Precipitation.

Light rains decrease visibility; therefore, less HC smoke is needed for concealment. Heavy rain and snow reduce visibility so that smoke is rarely necessary to provide concealment.

5. Cloud Cover.

When the sky is more than 70 percent covered with clouds, a neutral temperature gradient prevails. The atmosphere is moderately stable, and conditions are generally favorable for smoke.

6. Terrain.

Terrain will deflect or channel wind flow. The influences of terrain on wind flow (transport) are greatest with light winds and stable conditions and decrease with stronger winds and unstable conditions.

Since smoke is carried by the wind, it normally follows the earth's contours. On flat or unbroken terrain and over water, smoke streamers take longer to spread out and mix. On the other hand, trees and buildings tend to mix smoke streamers and increase smoke coverage. Large hill masses and rugged terrain cause strong crosscurrents which disperse smoke, causing holes and unevenness.

(a) Arctic.

Smoke operations in arctic regions or other cold weather areas present special problems common to all types of units. On clear days, stable conditions exist over snowy surfaces and are strongest about sunrise. Smoke tends to remain near the surface and may travel for long distances before dissipating. Under extremely cold conditions, smoke clouds last longer than under more temperate conditions. Snow or fog reduces visibility so that much less smoke is required for effective screening.

(b) Desert.

All deserts have certain characteristics in common -- lack of water, absence of vegetation, large areas of sand, extreme temperature ranges, and brilliant sunlight. Because of meteorological conditions and the vast areas usually available for dispersing and maneuvering troops, it is difficult to make beneficial use of smoke units. However, smoke can be used effectively for screening and deception. Smoke may be employed to screen an installation or the breaching of barriers and minefields and to cover artillery positions at night to reduce muzzle flash. Desert sands absorb heat from the sun and cause appreciable horizontal temperature differences which, in turn, may cause whirlwinds. The soil is heated during the day to such an extent that smoke operations become extremely difficult because of strong unstable conditions. Smoke tends to pillar because of rising air currents. High winds and dust storms occur throughout the year. Smoke is more effective in early morning and late evening, or on an overcast day when neutral atmospheric conditions exist.

(c) Mountain.

Mountain operations are characterized by the difficulties encountered due to terrain. Generally, inadequate road nets found in mountain areas enhance the military value of existing roads and add importance to high ground that dominates other terrain. Smoke generators can screen artillery positions, supply routes, and preparations for installations and entrenchments. It can also reduce the enemy's ability to use high ground for observation. Small smoke units are often required to operate for extended periods with limited resupply in mountain operations because of transportation difficulties. Steep hills split winds so they eddy around and over the hill. Thermally induced slope winds occur throughout the day and night. These conditions make it extremely difficult to establish and maintain a smoke screen. Wind currents, eddies, and turbulence must be continuously studied and observed.

(d) Jungle.

The jungle ordinarily affords concealment from air and ground observation. Smoke screens may be employed in jungle operations to screen aircraft landing areas, to prevent directed fire on helicopters approaching landing zones, and to screen landing zones while troops embark or debark.

Smoke used in dense vegetation tends to spread slowly downwind and downslope, and to follow creek beds and gullies. Jungle weather is usually hot, humid, and characterized by sudden changes. Windspeed in jungle areas normally does not exceed 3 kilometers per hour.

7. Night Operations.

Smoke can be used to an advantage in night operations. Obscuring smoke placed on the enemy at night interferes with his operations and with his observation of our operations. Some night vision devices are adversely affected. The efficiency of light intensification devices can be reduced by using smoke to reduce the usable light energy. Smoke used against armor materially reduces its movement, direct fire, and observation abilities. Any night employment of smoke must be judicious so as not to interfere with our own operations.

The main objective of night operations is to degrade the opposing force's infrared and image intensifying devices. On moonlit nights, smoke is needed to conceal and to deceive the enemy while obscuring their view from observation posts and overwatch positions. However, night operations have special problems. It is difficult to control the smoke screen and the noise of generators. Proper preparation of generator positions help night operations succeed. It takes longer to see if the smoke must be adjusted and its harder to make such adjustments in the dark.

APPENDIX B
TOXICITY TEST RESULTS

Table B-1. Toxic Effects in Humans Produced by Zinc Chloride Through Smoke Inhalation¹

| Exposure time | Concentration (mg/m ³) | CT dosage ^a (mg-min/m ³) | Effects |
|--------------------------|------------------------------------|---|--|
| 2 min | 80-120 | 160-240 | Nose, throat, and chest irritation; cough; nausea. |
| 9 min NA ^b | 190 NA | 1,700 to 2,000 | Marked throat irritation, some lung congestion, usually requiring hospitalization, observation, and treatment. |
| 5 min approx. | 4100 | 20,000 | Severe respiratory irritation leading to "chemical pneumonia," requiring aggressive treatment. |
| NA | NA | 50,000 | Massive respiratory tract injury, may be fatal, death due to shock & pulmonary edema. |

^a CT dosage = concentration x exposure time

^b NA = concentration and/or duration not specified

Table B-2. Effects of Zinc Chloride in Experimental Animals

| Route of administration | Dose | Length of exposure | Effects |
|--|---------------------------------|--------------------|--|
| Acute Effects <u>Inhalation (Acute Effects)</u> Dogs | NA ^a | 20 minutes | Hemoconcentrations, mottled pulmonary edema extending over the whole of both lung fields |
| Mice | 11,800 mg-min/m ³ | NA | LCt50 ^b |
| <u>Percutaneous Application</u> Guinea pigs | 2 ml of 0.239M aqueous solution | Single dose | Reduced weight gain |
| <u>Intraperitoneal Injection</u> Guinea pigs | 2 ml of 0.239M aqueous solution | Single dose | 6/10 mortalities within 24 hr, 2 more deaths by day 7 |
| Rats | 100 mg/kg | Single dose | Average lethal dose |
| <u>Ocular Application</u> Rabbits | 50% zinc chloride solution | Single dose | Corneal opacification, corneal ulceration and perforation, some discharge |
| <u>Oral Administration</u> Mice | 350 mg/kg | Single dose | LD50 ^c |
| Rats | 350 mg/kg | Single dose | LD50 |
| Guinea pigs | 200 mg/kg | Single dose | LD50 |
| Rats | 750 mg/kg | Single dose | Average lethal dose |
| Rabbits | 1000 mg/kg | Single dose | Average lethal dose |
| <u>Subcutaneous Injection</u> Rats | 1000 mg/kg | Single dose | Average lethal dose |

Table B-2 cont'd

| Route of administration | Dose | Length of exposure | Effects |
|--|-----------------------------|--|---|
| <u>Oral Administration</u> Rats | 0.25-0.5% | Chronic (duration of administration not specified) | No effect. |
| Rats | 4-6 mg in olive oil | Daily for 20 weeks | Rusting or greying of coat; crusting of the nose, chin, tail, eyelids; severe alopecia; growth retardation. Symptoms resembled pantothenic acid deficiency. |
| <u>Intraperitoneal Injection</u> Rats | 1.2 mg in normal saline | Alternate days for 20 days | Modifications of epithelium of loops of Henle, distal and proximal convoluted tubules, lysed cells due to nuclear eruption, vacuolized cytoplasm. |
| Rats | 0.6-1.2 mg in normal saline | Alternate days for 20 days | Temporary paresis of hind legs and anal sphincters, morphological changes of motor neurons of spinal cord. |

a Not available

b Median lethal dosage (concentration x exposure time)

c Median lethal dose

Table B-3. Tumor Development in Mice After Administration of Zinc Chloride in Drinking Water for 5-8 Months

| Group | Number of animals | Zinc chloride concentration (mg/l) | Number of animals with tumors | Pathological findings |
|-----------------------|-------------------|------------------------------------|-------------------------------|---|
| I^a | | | | |
| Experimental | 100 | 10-20 | 10 | Seminoma, bone marrow, and uterine cancer ^b |
| Control | 40 | 0.016 mg/l zinc | 0 | Hepatic and suprarenal necrosis |
| II^c | | | | |
| Experimental | 75 | 10-20 | 9 | Pulmonary adenoma, hemangioma, uterine and bone marrow cancer |
| Control | 25 | 0.016 mg/l zinc | 2 | Pulmonary adenoma, hemangioma |
| III | | | | |
| Experimental | 100 | 10-20 mg + cigarette smoke | 4 | Pulmonary adenoma, lung, mammary, and uterine cancer |
| Control | 50 | Cigarette smoke only | 1 | Pulmonary adenoma, epithelial metaplasia of bronchial mucosa |

^a Tumor-resistant strain of mice

^b Type of uterine cancer not specified

^c Offspring of tumor-susceptible mice

^d Animals were maintained in a glass cage saturated with cigarette smoke.

Table B-4. Acute Aquatic Toxicity (TL50 Values) of Zinc to Several Species of Fish in Water of Various Water Qualities

| Species | Size | Compound | Exposure time (hr) | Exposure type* | Temperature (°C) | Concentration (mg/l) | pH | Hardness (alkalinity) | Ref |
|--|-------------------------|--------------|----------------------|---------------------|------------------------|--|---------|-----------------------|-----|
| Rainbow trout | 7 gm | Zinc | 96 | FT | 11.6-12.4 | 0.10 Zn | 6.8-7.0 | 20-25 (17-26) | ** |
| Rainbow trout | 1.5 gm | Zinc | 96 | S | 10 | 0.09 Zn | 7 | 20 (20) | 2 |
| Rainbow trout | - | Zinc | 48 | S | 15 | 3.2 Zn | 7.6 | 300 (200) | 3 |
| Cutthroat trout (<u>Salmo clarki</u>) | - | Zinc | 24 48 96 24 | FT FT FT S | 1 | 0.62 Zn 0.27 Zn 0.09 Zn 0.42 Zn | 7 | - (23.9) | 4 |
| Chinook salmon (<u>Oncorhynchus tshawytscha</u>) | At hatch 1 month old | Zinc Zinc | 96 96 | FT FT | 11.1-12.0 10.8-12.5 | >0.70 Zn 0.103 Zn | 6.8-7.0 | 20-25 (17-26) | ** |
| Atlantic salmon (<u>Salmo salar</u>) | Juveniles | Zinc | 24 | FT | 15 | 0.65 Zn | 7.1-7.5 | 20 (-) | 4 |
| Fathead minnow | 45 (mm) | Zinc | 24 48 96 | S | 23.2 | 8.9 Zn 7.8 Zn 7.6 Zn | 6.2 | 166 (-) | 6 |

Table B-4 cont'd

| Species | Size | Compound | Exposure time (hr) | Exposure type* | Temperature (°C) | Concentration (mg/l) | pH | Hardness (alkalinity) | Ref |
|---|---------|-----------------------------------|--------------------|----------------|------------------|------------------------|-----|-----------------------|-----|
| Bluegills | 1-2 gm | ZnCl ₂ | 24 | S | 15 | 7.24 ZnCl ₂ | 7.5 | 20 (18) | 7 |
| | | | 48 | | | 5.76 ZnCl ₂ | | | |
| | | | 96 | | | 5.37 ZnCl ₂ | | | |
| Banded killifish <u>Fundulus diaphanus</u> | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 17 | 22.6 Zn++ | 7.8 | 53 (-) | 8 |
| | | | 48 | | | 20.7 Zn++ | | | |
| | | | 96 | | | 19.1 Zn++ | | | |
| Banded killifish | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 28 | 23.0 Zn++ | 8.0 | 55 (-) | 9 |
| | | | 48 | | | 20.4 Zn++ | | | |
| | | | 96 | | | 19.2 Zn++ | | | |
| Striped bass <u>Morone saxatilis</u> | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 17 | 11.2 Zn++ | 7.8 | 53 (-) | 8 |
| | | | 48 | | | 10.0 Zn++ | | | |
| | | | 96 | | | 6.7 Zn++ | | | |
| Striped bass | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 28 | 11.3 Zn++ | 8.0 | 55 (-) | 9 |
| | | | 48 | | | 10.0 Zn++ | | | |
| | | | 96 | | | 6.8 Zn++ | | | |
| Pumpkinseed <u>Lepomis gibbosus</u> | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 17 | 25.2 Zn++ | 7.8 | 53 (-) | 8 |
| | | | 48 | | | 21.8 Zn++ | | | |
| | | | 96 | | | 20.0 Zn++ | | | |

Table B-4 cont'd

| Species | Size | Compound | Exposure time (hr) | Exposure type* | Temperature (°C) | Concentration (mg/l) | pH | Hardness (alkalinity) | Ref |
|---|---------|-----------------------------------|--------------------------|-------------------|---------------------|-------------------------|-----|--------------------------|-----|
| Pumpkinseed | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 28 | 25.1 Zn++ | 8.0 | 55 (-) | 9 |
| | | | 48 | | | 21.9 Zn++ | | | |
| | | | 96 | | | 20.1 Zn++ | | | |
| White perch <u>Roccus americanus</u> | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 17 | 13.6 Zn++ | 7.8 | 53 (-) | 8 |
| | | | 48 | | | 10.2 Zn++ | | | |
| | | | 96 | | | 14.3 Zn++ | | | |
| White perch | ≥ 20 cm | Zn(NO ₃) ₂ | 24 | S | 28 | 13.5 Zn++ | 8.0 | 55 (-) | 9 |
| | | | 48 | | | 10.1 Zn++ | | | |
| | | | 96 | | | 14.4 Zn++ | | | |

75

*Exposure type: FT = flow through, S = static

**Chapman, G. A. Unpublished data available at the National Water Quality Laboratory, Duluth, Minnesota.

Table B-5. Toxic Effects of Zinc Chloride to Freshwater
and Marine Organisms¹

| Concentration (mg/l) | Duration of exposure (hr) | Species | Effects produced |
|------------------------------------|------------------------------|---|------------------------------------|
| <u>Freshwater</u> | | | |
| 4.3 | 96 | Nitzschia linearis | LC50 ^a |
| 0.79-1.27 | 96 | Physa heterostropha | LC50 |
| 1.5 | 64 | Daphnia magna | Minimum lethal concentration |
| 0.3 | 96 | Lebistes reticulatus (common guppy) | Minimum lethal concentration |
| 20-22 | 48 | Tilapia mossambica | LC100 ^b |
| 10-15 | 48 | Tilapia mossambica | LC50 |
| 5 and 2 mg/l dissolved oxygen | 96 | Lepomis macrochirus (bluegill sunfish) | LC50 |
| 8 and 8-9 mg/l dissolved oxygen | 96 | Lepomis macrochirus | LC50 |
| 1 | 24 | Cyprinus carpio | Killed |
| 17.1 | 1 | minnows (species not available) | No effect |
| 0.14 | 50 | Anquilla rostrata (juvenile eel) | Maximum tolerated concentration |
| 0.65 (as zinc) | 12 | Anquilla rostrata | Killed |
| 0.17 | NAC ^c | Etheostoma histrio (harlequin fish) | LC50 |
| 157-180 | 2 | Fundulus heteroclitus (Mummichog) | Became sluggish |
| 157-180 | 24-48 | Fundulus heteroclitus | Killed |
| 66 | 48-192 | Fundulus heteroclitus | LC50 |

Table B-5 cont'd

| Concentration (mg/l) | Duration of exposure (hr) | Species | Effects produced |
|-------------------------|------------------------------|--|--|
| 43 | 192 | <i>Fundulus heteroclitus</i> | Tolerable concentration |
| 5.2 | 48 | <i>Lepomis macrochirus</i> | LC50 |
| 2.86-3.78 | 96 | <i>Lepomis macrochirus</i> | LC50 |
| 7.24 | 24 | <i>Lepomis macrochirus</i> | LC50 |
| 7.24 | 48 | <i>Lepomis macrochirus</i> | LC50 |
| 5.37 | 96 | <i>Lepomis macrochirus</i> | LC50 |
| < 12 | 336 | <i>Ictalurus nebulosus</i> (Brown bullhead) | No effects |
| 8.0 | 96 | <i>Brachydanio rerio</i> (adult) | No effects |
| 28.0 | 48 | <i>Brachydanio rerio</i> (adults) | LC50 |
| 105.0 | 48 | <i>Brachydani rerio</i> (eggs) | LC50 |
| 10.0 | 48 | Minnows (species not reported) | Killed |
| 16.0 | 20 | <i>Anquilla</i> sp. (eels) | Killed |
| 100 | 96 | Fish (species not reported) | No mortalities |
| 200 | 48 | <i>Fundulus heteroclitus</i> | Killed in fresh- water; no mortalities in seawater |
| 1000 | 24 | Trout (species not reported) | Killed |
| 7.45 | 96 | <i>Lepomis macrochirus</i> (small) | LC50 |

Table B-5 cont'd

| Concentration (mg/l) | Duration of exposure (hr) | Species | Effects produced |
|-------------------------------------|---------------------------|---|---|
| 7.20 | 96 | <i>Lepomis macrochirus</i> (average) | LC50 |
| 6.91 | 96 | <i>Lepomis macrochirus</i> (large) | LC50 |
| <u>Marine</u> | | | |
| 0.17 | 42-48 | <i>Mercenaria mercenaria</i> (hard clam) | LC50 |
| 0.25 | 42-48 | <i>Mercenaria mercenaria</i> | Concentration causing 100% mortality |
| 0.9-1360 | 6,18,24 | <i>Dendraster excentricus</i> (sand dollar) | Abnormal cleavage; abnormal development patterns |
| 2.5-10 mg/l | 17 | <i>Arbacia punctulata</i> (sea urchin) | Inhibition of gastrulation, persistent fertilization membranes; death-especially at high concentrations; abnormal development |
| 100 mg/l alternating with sea water | 5 minute intervals | <i>Arbacia punctulata</i> (sea urchin) | Abnormal development; persistent fertilization membranes |
| 0.14-13.6 | NA | <i>Paracentrotus lividus</i> (sea urchin) | Lysis, abnormal and delayed development |

^a LC50 - median lethal concentration

^b LC100 - lethal concentration at which 100% died

^c NA - not available

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| | | OUTSIDE AGENCIES | |
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| | | Battelle, Columbus Laboratories ATTN: TACTEC 505 King Avenue Columbus, OH 43201 | 1 |

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Los Alamos National Laboratory
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ADDITIONAL ADDRESSEES

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ATTN: DELEW-M-T-AC (Ms Arthur)
White Sands Missile Range, NM 88002

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USA Mobility Equipment Research and
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Creative Optics
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McDonnell Douglas Astro Co
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Dr. W. Michael Farmer, Assoc Prof, Physics
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ARNG
Operating Activity Center
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Aberdeen Proving Ground, MD 21010

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USA Environmental Hygiene Agency
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ATTN: Librarian, Bldg 2100
Aberdeen Proving Ground, MD 21010

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